

**The origin and evolution of granites:  
an in-situ study of zircons from  
Scottish Caledonian intrusions**

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## **Declaration**

This thesis is entirely my own work except where indicated otherwise.

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# Abstract

Granitic magmatism in collision belts is widely regarded as a major mechanism for generating continental crust. This hypothesis can be tested by identifying the source rocks of granitic magmas, and in particular the contribution by pristine mantle material. The complexity of granites, and their susceptibility to post-crystallisation alteration, has until recently provided a major obstacle to progress. Zircon, a common and chemically robust accessory mineral in granitoid rocks, retains a record of the composition of the magma it grew from. Recent developments in micro-analysis (ion microprobe and laser ablation ICP-MS) now enable in-situ analysis of zircon crystals at high spatial resolution and precision, providing access to this record at the previously inaccessible intra-crystal scale. The resulting data have enormous potential to provide new insights into the nature and age of source rocks and the processes driving magma evolution. This project used an integrated in-situ O, U-Pb and Hf isotope, trace and rare earth element study of zircon to identify the sources and chart the evolution of two ‘I-type’ (igneous/infracrustal precursor) Scottish late Caledonian (~430-400 Ma) granite plutons. I have constrained models of magma generation, the relative contributions of mantle and crust, the ages and identities of their lower crustal sources, and have shown that the plutons played, at most, a minor role in crustal growth. In addition, I have been able to resolve the extent to which open-system changes like magma mixing affected the magma compositions. The same approach was used in a pilot study of three Caledonian (~460 Ma) ‘S-type’ (sedimentary/supracrustal precursor) granite plutons, which theoretically represent magmas formed by melting of a purely supracrustal source. The data confirm that Dalradian country rocks were the primary source, but reveal remarkable isotopic diversity within and amongst the three plutons. The most important general conclusion from this PhD study is that the complexity and scale of isotopic heterogeneity between plutons, amongst samples of the same pluton, in single samples and within individual crystals is far greater than previously recognised, consistent with the incremental assembly of plutons from multiple melt batches of differing composition, sources and petrogenetic evolution.

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**I.**

## **Introduction**

# Introduction

## 1. Introduction

The formation of the Earth's crust is widely envisaged to be at least a two-stage process involving generation of basaltic magmas by melting of the mantle and subsequent production of more evolved magmas such as granites by either differentiation or re-melting of basaltic magmas (Kelemen, 1995; Rudnick, 1995). Differentiation is thought to occur within large magma chambers, which ascend rapidly through the crust by diapirism or stoping until they reach shallow crustal levels where they are either emplaced as plutons or form sub-volcanic magma chambers (e.g. Buddington, 1959; Paterson et al., 1996; Petford et al., 2000; Pitcher and Berger, 1972).

Granites are widely viewed as the end-products of growth of the Earth's crust either directly from mantle-derived magmas or by re-melting of pre-existing crust (e.g. Atherton and Petford, 1993; Chappell and White, 2001; Gill, 1981; Grove et al., 2002, 2003; Grove and Kinzler, 1986; Izbekov et al., 2004; Müntener et al., 2001; Musselwhite et al., 1989; Petford and Atherton, 1996; Prouteau and Scaillet, 2003; Rapp and Watson, 1995; Rogers and Hawkesworth, 1989; Smith and Leeman, 1987; Tepper et al., 1993). In order to understand processes of crust formation and the evolution of the continental crust, granites from different locations and tectonic settings and of varying ages have been studied for many decades. A principal aim of granite research has been to identify granite sources, and in particular the contribution made by the mantle.

Previously it has been suggested that granites have simple petrogenetic histories and comprise either igneous/intracrustal (I-types) or sedimentary/supracrustal (S-types) sources (Chappell and White, 1974). However, after much further research, the development of new analytical techniques and improved precisions of conventional techniques, it has been shown that in reality the majority of granites comprise multiple sources (John and Wooden, 1990; Kemp et al., 2007; Kemp and Hawkesworth, 2003; Miller et al., 1990), which leaves the relationship between granite genesis and crustal growth unresolved.

While the origin of S-type granites by melting of crustal sedimentary rocks is widely accepted, the origin of I-type granites is much more complicated and controversial. The latter may represent mixtures of melts of different (crustal or mantle) origins, may contain unmelted or partially melted remnants of their sources, and may have evolved and differentiated extensively from their parental mafic melts. Furthermore, whole-rock geochemical studies of granites have been complicated by their susceptibility to post-crystallisation alteration by fluid-rock exchange, in particular the usually abundant feldspars (e.g. King and Valley, 2001; Taylor and Huston, 1998; Valley and Graham, 1996); whole-rock data commonly do not represent the magma composition from the time of crystallisation, and may lead to incorrect interpretations and models.

In recent years studies using the mineral zircon ( $\text{ZrSiO}_4$ ), a common accessory phase in granitoid rocks, have made significant contributions to our understanding of the origin and evolution of granites, and hence of the continental crust (e.g. Coleman et al., 2004; Hawkesworth and Kemp, 2006a, b; Kemp et al., 2007; Matzel et al., 2006). Zircon has been widely used to determine the U-Pb crystallisation ages of granitic rocks (e.g. Pidgeon and Aftalion, 1978; Pidgeon and Compston, 1992). As zircon is resistant to chemical modification following crystallisation, even at magmatic temperatures, it also contains a wealth of further information about the origin and evolution of its host granite. Due to its significant concentrations of U, Th, Hf, trace and rare earth elements (REEs) (ppm to percent level) (Kinny and Maas, 2003) it is suitable not only for U-Pb dating, but also for oxygen and Hf isotope, and trace element/REE analyses, which may be used to trace the entire petrogenetic history of the host granite from genesis to post-crystallisation alteration. Zircon crystals may now be analysed in-situ at high spatial resolution and precision by ion microprobe (SIMS) and laser ablation ICPMS. Due to the high spatial resolution of these techniques multiple analyses may be made within a single crystal, providing information about previously inaccessible intra-grain changes in composition. In addition, as SIMS analysis consumes only very small amounts of sample material oxygen, U-Pb isotope, trace elements/REEs and Hf isotopes can be measured in exactly the same area enabling direct correlation of the data sets.

In this PhD study, I have applied these new micro-analytical techniques to zircons of Scottish Caledonian I- and S-type granite plutons. Even though this classic granite suite has been studied extensively over the last four decades the sources and petrogenesis of the voluminous late Caledonian (~430-400 Ma) I-type granites in particular, and hence their role in crustal growth remain largely unresolved due to the limitations of whole-rock data. The objectives of this study were to:

- Constrain the ages and origins of selected Scottish Caledonian granite plutons. Characterise their mantle and/or lower crustal sources.
- Test models of lower crustal age and composition beneath the Scottish Highlands.
- Evaluate the contribution of these voluminous magmas to continental growth.
- Use information stored in zircon to test existing models and provide new insights into granite genesis, ascent and emplacement.

## **2. The origin and evolution of granites – previous and recent models**

### *2.1. Granite sources*

In order to establish a link between granite magmatism and crustal growth, the main aim of past and ongoing granite research has been to identify the sources of granites, and in particular to constrain the proportion of primitive mantle-derived versus crustal material. Chappell and White (1974) conducted an extensive whole-rock study of granites in the Lachlan Fold Belt (LFB) of southeastern Australia, based on which they proposed that granites are derived from either an igneous/infracrystal (I-types) or a sedimentary/supracrustal source (S-types), which can easily be distinguished by whole-rock geochemical and isotopic compositions, and major and accessory phase assemblage (see Table 1 for characteristics of I- and S-type granites). They further suggested that granitoid rocks inherit their geochemical composition and possibly even some petrographic features from their source, and closely reflect the composition of the latter.



**Table 1**  
**Characteristics of I- and S-type granites (Chappell and White, 2001)**

I-type granites	S-type granites
relatively high Na, Na <sub>2</sub> O typically > 3.2 % in felsic varieties decreasing to > 2.2 % in mafic samples	relatively low Na, Na <sub>2</sub> O typically < 3.2 % in rocks with c. 5 % K <sub>2</sub> O, decreasing to < 2.2 % in rocks with c. 2 % K <sub>2</sub> O (due to removal of Na into sea water (or evaporites) during sedimentary fractionation)
Mol. Al <sub>2</sub> O <sub>3</sub> /(Na <sub>2</sub> O+K <sub>2</sub> O+CaO) < 1.1	Mol. Al <sub>2</sub> O <sub>3</sub> /(Na <sub>2</sub> O+K <sub>2</sub> O+CaO) > 1.1
CIPW normative diopside or < 1 % normative corundum	> 1 % CIPW normative corundum
broad spectrum of compositions from felsic to mafic	relatively restricted in composition to high SiO <sub>2</sub> types
regular inter-element variations within plutons; linear or near-linear variation diagram	variation diagrams more irregular
hornblende common	muscovite, up to 35 % biotite (in more mafic S-types), garnet and cordierite common, no hornblende
sphene; apatite inclusions in biotite and hornblende	monazite, apatite in larger discrete crystals
( <sup>87</sup> Sr/ <sup>86</sup> Sr) <sub>i</sub> = 0.704-0.706 (McCulloch and Chappell (1982) report values of up to 0.711)	( <sup>87</sup> Sr/ <sup>86</sup> Sr) <sub>i</sub> > 0.708
mafic hornblende-bearing igneous xenoliths	metasedimentary xenoliths

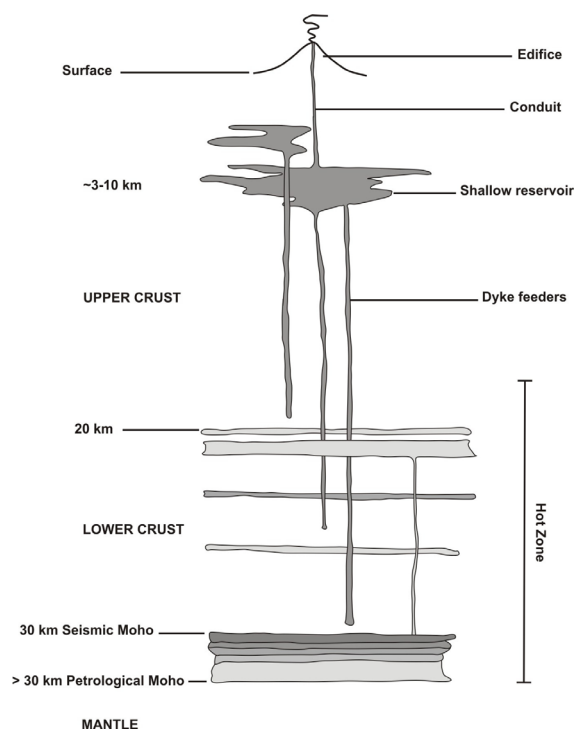


Fig. 1: Deep crustal hot zone model (after Annen et al., 2006). See text for description.

Since then, numerous whole-rock geochemical and isotopic studies of the LFB granites and other granites worldwide have shown that in reality the majority of intrusions display to some extent the characteristics of both I- and S-type granites, and appear to comprise multiple sources (e.g. Chappell et al., 1987, 2000; Collins, 1998, 1999; Kemp and Hawkesworth, 2003; Vernon, 1983; Wall et al., 1987). This has recently been confirmed for selected LFB I-type granites (Cobargo, Jindabyne and Why Worry suites) by an integrated in-situ oxygen and Hf isotope study of zircons, which was able to demonstrate that these intrusions were formed by interaction (magma mixing or assimilation) between mantle-derived juvenile and supracrustal materials (Kemp et al., 2007), and were not solely sourced from the mantle or igneous precursors. Another important outcome of this study was that by using an integrated micro-analytical approach it was possible to show that the I-type granites incorporate between 50 % and 85 % pristine contemporaneous mantle material, and hence have made a significant contribution to Lower Palaeozoic continental crustal growth.

## *2.2. Melt generation, ascent and emplacement*

The generation of intermediate and silicic magmas has been widely considered to occur predominantly in the crust or close to the Moho by differentiation of mantle-derived basalt or basaltic andesite (e.g. Gill, 1981; Grove et al., 2002, 2003; Grove and Kinzler, 1986; Müntener et al., 2001; Musselwhite et al., 1989; Prouteau and Scaillet, 2003; Rogers and Hawkesworth, 1989) and by partial melting of pre-existing crustal rocks following mafic underplating (e.g. Atherton and Petford, 1993; Chappell and White, 2001; Izbekov et al., 2004; Petford and Atherton, 1996; Rapp and Watson, 1995; Smith and Leeman, 1987; Tepper et al., 1993). The depths at which chemical differentiation, magma mixing or melting and assimilation take place are not well constrained; the traditional view has been that these processes predominantly occur in crustal magma chambers. These are envisaged as large bodies of magma, which ascend rapidly through the crust by diapirism or stoping (e.g. Buddington, 1959; Paterson et al., 1996; Petford et al., 2000; Pitcher and Berger, 1972), and are either emplaced as plutons or form sub-volcanic reservoirs.

However, a number of problems have been identified with these traditional and relatively simple models. (1) Even though the existence of some ephemeral shallow sub-volcanic magma chambers has been proven, seismic techniques have failed to locate large bodies of magma (e.g. Detrick et al., 1990). (2) To produce intermediate and silicic magmas, which in large batholiths may occupy hundreds to thousands of km<sup>3</sup>, approximately twice as much primary mantle-derived magma has to undergo fractional crystallisation (Foden and Green, 1992; Müntener et al., 2001). However, this would also produce huge amounts of mafic cumulates of which to date no evidence has been found. (3) Thermal modelling has demonstrated that it is difficult to maintain even small permanent magma chambers in a molten state in the cold shallow crust, and that high rates of magma replenishment would be required (e.g. Lister, 1983). (4) The diapiric ascent of magma is too slow and energetically inefficient to be geologically important (e.g. Clemens and Mawer, 1992; Petford et al., 2000), and stoping is not volumetrically significant in the emplacement of most plutons (Glazner and Bartley, 2006).

Recent thermal models suggest that ‘deep crustal hot zones’ may play an important role in the generation of intermediate and silicic igneous rocks (Annen et al., 2006; Annen and Sparks, 2002). The development of these hot zones results from repeated intrusion of mantle-derived hydrous basalt sills into the lower and/or middle crust, where melts are generated either by (1) differentiation of the basalt to produce residual and more siliceous H<sub>2</sub>O-rich melts, by (2) mixing between silicic melts, possibly generated by partial melting of crustal rocks (e.g. Druitt et al., 1999), and mantle-derived mafic magmas, or by (3) partial melting of pre-existing crustal rocks including early basalt sills or older mafic lower crust (Fig. 1). Mixing of residual melts (or mafic mantle melts) and crustal partial melts creates a large range of intermediate and silicic melts. Thus, the ‘deep crustal hot zone model’ provides a conceptual framework and theoretical underpinning for models of mafic underplating (Raia and Spera, 1997), basalt differentiation near the Moho (Gill, 1981; Grove et al., 2002), and assimilation and fractional crystallisation (AFC) (e.g. DePaolo, 1981). The efficiency of melt production in deep crustal hot zones largely depends on the amount of intruding basalt, spacing of the basalt sills, the level of emplacement in the crust, the rate of emplacement and the composition of lower and middle crust.

Residual melts are most efficiently produced by differentiation of basalt at deep crustal levels. However, in the model of Annen et al. (2006) the largest amounts of crustal partial melts are generated either by random basalt sill injection over extended periods of time at different mid- and lower crustal levels, heating the crust from below and above, or by emplacement of sills at the contact with a fertile upper crust. After melt generation, the melts segregate and, depending on their H<sub>2</sub>O content, density, viscosity and ascent path, ascend more or less rapidly into shallow reservoirs where they undergo crystallisation by degassing and cooling. Entrained material from the source will be partially or entirely digested, but contamination by xenocrystic wall-rock material may occur during ascent (Annen et al., 2006). Melt extraction is generally envisaged to take place in pulses, their frequency being dependent on the timescales of melt generation and segregation (Annen et al., 2006; Bons et al., 2004). Thus, magma reservoirs and plutons are thought to grow by incremental assembly of melt batches of commonly differing composition (Annen et al., 2006).

The 'deep crustal hot zone' model is in good agreement with a growing body of field and geochronological evidence, which suggests that some (and perhaps most) plutons were emplaced incrementally as a series of sheet- or dyke-like intrusions over time spans an order of magnitude longer than the thermal lifetime of large magmatic masses and never existed as a large molten magma body (Brown and McClelland, 2000; Coleman et al., 1995; Wiebe, 1993; Wiebe and Collins, 1998). For example, TIMS dating of the Tuolumne Intrusive Suite in California demonstrated that it was incrementally assembled over a period of at least 10 m.y. (Coleman et al., 2004). In addition, a recent detailed TIMS study of the Mount Stuart batholith located in the North Cascades of Washington State was able to resolve that it was constructed by four major magma pulses over a period of ~5.5 m.y. (Matzel et al., 2006). Contacts between different magma batches may be sharp, gradational or cryptic depending on the time between injection events and the degree of homogenisation by post-emplacement annealing (Glazner et al., 2004). Hence, the chemical heterogeneity previously interpreted to result from fractional crystallisation (e.g. Bateman and Chappell, 1979; Sisson and Moore, 1994; Tindle and Pearce, 1981) and/or magma mixing (Frost and Mahood, 1987; Kistler et al., 1986) in large

magma chambers, might reflect processes operating at much deeper levels (Glazner et al., 2004), for example in deep crustal hot zones.

### **3. The Scottish Caledonian granites**

The majority of the classic Scottish Caledonian I- and S-type granites are located in the Grampian terrane of the Scottish Highlands (**Fig. 2**) where they intruded metasedimentary rocks of the Dalradian Supergroup, a c. 25 km thick sequence of deformed and metamorphosed late Neoproterozoic to Lower Ordovician shallow- and deep-water sediments and volcanics (Harris et al., 1978, 1994; Stephenson and Gould, 1995). The Caledonian granites are in many respects (e.g. emplacement age, occurrence of both I- and S-type granites) similar to the LFB granites of southeastern Australia. However, in the LFB I- and S-type granites intruded contemporaneously (~450-340 Ma) (Gray and Foster, 1997) and share several chemical features, which led to the interpretation that their generation was coupled and involved melting of similar source materials (Kemp and Hawkesworth, 2003). In contrast, the Caledonian I- and S-type granites intruded at different times (S-types: ~470-465 Ma; I-types: 430-400 Ma) and involved different sources.

The Caledonian S-type granites are thought to have been produced by melting of a supracrustal source, most likely the Dalradian country rocks (Harris et al., 1978, 1994; Stephenson and Gould, 1995), and to date no evidence exists for the involvement of infracrustal or mantle-derived components. The origin and sources of the late Caledonian I-type granites have caused much debate and are still not fully resolved. Proposed models suggest that the granites were predominantly derived from the mantle (Brown and Locke, 1979; Simpson et al., 1979), from the crust (Hamilton et al., 1980; Leake, 1978; Pankhurst, 1979; Pidgeon and Aftalion, 1978; Pitcher and Berger, 1972), or from mixed sources comprising mantle and crustal components (Clayburn et al., 1983; Frost and O’Nions, 1985; Halliday, 1984; Halliday et al., 1979, 1980, 1984; Harmon and Halliday, 1980); the latter model is generally favoured today. However, little is known about the composition of the mantle and lower crustal basement beneath the Grampian terrane; thus the identities

and compositions of the sources and their relative contributions to granitic magmas have not been constrained.

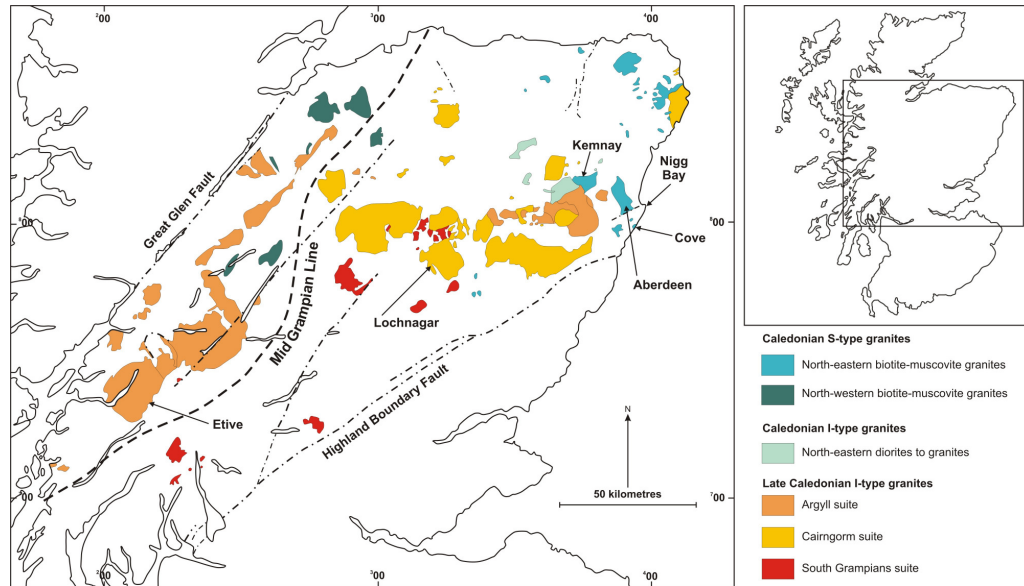


Fig. 2: Map of the Grampian terrane (located between Great Glen and Highland Boundary faults) in Scotland showing the locations of the Caledonian I- and S-type granites and of the plutons studied in this PhD project (after Stephenson and Gould, 1995).

### 3.1. The Caledonian S-type granites

The Caledonian S-type granites intruded contemporaneously with and subsequent to the Grampian Event, which occurred between c. 480 Ma and 465 Ma (Oliver, 2001) and resulted from the collision of the Laurentian continental margin with a southeast-dipping subduction zone and a volcanic arc that developed during closure of the Iapetus Ocean. Evidence of the volcanic arc was found in western Ireland (South Mayo Trough) (Dewey and Ryan, 1990); indirect evidence for the existence of this arc was discovered in the Midland Valley of Scotland, buried underneath the post-Caledonian sedimentary cover (Bluck, 1983, 1984). The Grampian Event is considered to be the main tectonic and metamorphic event in the Grampian Highlands, involving overthrusting of an ophiolite nappe, regional deformation and

Barrovian metamorphism of the Dalradian metasedimentary rocks (Dewey and Ryan, 1990; Dewey and Shackleton, 1984).

The Grampian Event was accompanied by syn- and late-tectonic plutonism. This included mafic and ultramafic plutons - the 'Newer Gabbros' (Read, 1961), and two suites of syn- to late-tectonic diorites and granites (Strachan et al., 2002). The majority of granites are peraluminous, have high initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios ( $> 0.71$ ), contain a high proportion of country rock xenoliths and older inherited zircons, and have thus been interpreted as S-type granites (Harmon, 1983; Pankhurst, 1974; Pidgeon and Aftalion, 1978); few intrusions show I-type characteristics (Oliver et al., 2000). The S-type granites were probably produced by melting of Dalradian Supergroup country rocks at structural levels not far below the present level of exposure (Kneller and Aftalion, 1987; Richardson and Powell, 1976). The heat required for melt generation was most likely provided by crustal thickening and Barrovian metamorphism following arc-continent collision, aided in the Buchan area of the northeast Scottish Highlands by intrusion of the 'Newer Gabbros' (Oliver, 2001).

### *3.2. The late Caledonian I-type granites*

Following the Grampian Event (465 Ma to 435 Ma) the Grampian terrane experienced cooling, isostatic uplift and decompression (Dempster et al., 1995; Dewey and Mange, 1999; Oliver, 2001; Oliver et al., 2000; Soper et al., 1999). Closure of the Iapetus Ocean culminated in the collision of Laurentia, Baltica and Avalonia (Pickering et al., 1988; Soper et al., 1992; Soper and Hutton, 1984). At approximately 435 Ma oblique collision of Baltica and Laurentia resulted in the Scandian Event; this caused major ductile thrusting, folding and metamorphism within the Northern Highland terrane (Coward, 1990; Dallmeyer et al., 2001; Dewey and Mange, 1999; Kinny et al., 2003; Strachan et al., 2002), however in the Grampian terrane its effects appear to have been limited to large-amplitude folding and brittle faulting. Between c. 430 Ma and 400 Ma, broadly contemporaneous with - and subsequent to - the Scandian Event, the late Caledonian I-type granites were emplaced into Dalradian metasediments of the Grampian terrane (Oliver, 2001;

Rogers and Dunning, 1991; Stewart et al., 2001). Recent age dating has shown that the main phase of emplacement took place at approximately  $425 \pm 5$  Ma (Fraser et al., 2004; Rogers and Dunning, 1991). However, the connection between the collision and the voluminous I-type magmatism is unclear.

The predominantly shoshonitic and high-K calc-alkaline Caledonian I-type plutons have geochemical features typical of modern continental arcs, with the majority showing a metaluminous affinity (except for granites with  $> 70$  wt%  $\text{SiO}_2$ , which are peraluminous) (Frost et al., 2001). They are commonly hornblende-bearing (Soper, 1986) and contain high Rb/Sr and K/Na, low K/Rb and relatively low initial Sr ratios (0.704-0.708) (Halliday et al., 1985; Oliver et al., 2001; Stephens, 1988; Thirlwall, 1988). Previously they have been interpreted to have formed above an Andean-style subduction zone that dipped beneath the Laurentian continental margin (Brown, 1991; Brown et al., 1985; Oliver, 2001; Soper, 1986; Stephens and Halliday, 1984; Stephenson et al., 1999; Thirlwall, 1981, 1982, 1988). However, due to temporal, spatial and chemical discrepancies between the late Caledonian I-type plutons and typical subduction-related melts, this model has recently been challenged and an alternative slab-breakoff model has been proposed (Atherton and Ghani, 2002). The exact tectonic setting that led to emplacement of the late Caledonian I-type granites in Scotland remains controversial.

On the basis of whole-rock geochemical and isotopic data, the late Caledonian I-type granites have been subdivided into three distinct granite suites - the Argyll, Cairngorm and South Grampians suites (Stephens and Halliday, 1984). The *Argyll suite* consists of hornblende-biotite granodiorite and biotite granodiorite plutons with minor dioritic, appinitic and monzogranitic components (Stephens and Halliday, 1984; Strachan et al., 2002). The plutons are strongly metaluminous and are enriched in Ba, Sr and Na relative to the plutons of the other suites, whereas Nb, Th and Rb are present only at low concentrations (Fowler et al., 2001; Halliday, 1984; Halliday et al., 1985; Stephens and Halliday, 1984; Tarney and Jones, 1994; Thirlwall, 1988). The *Cairngorm suite* consists almost entirely of biotite monzogranite, which varies texturally between microgranite and coarse-grained, K-feldspar megacrystic granite. The intrusions contain high concentrations of Rb, Nb, Th and U, but have low Ba, Sr, Ti, P contents (Stephens and Halliday, 1984) relative to the Argyll suite. The *South*



*Grampians suite* is dominated by diorites, granodiorites and monzogranites, and comprises a higher proportion of gabbroic and appinitic intrusions than the other suites. In general, this suite is strongly metaluminous with higher K and Th abundances than the Argyll suite, but lower concentrations of Zr, La, Ce, Ba and Rb (Stephenson et al., 1999).

To date the compositional differences between the suites are not fully understood; they may reflect heterogeneities in the composition and age of the underlying lower crustal basement and/or mantle, or differences in the relative mantle and crustal contributions. Halliday (1984) proposed the existence of an important boundary in the deep basement and possibly in the mantle beneath the Grampian terrane separating the Argyll suite plutons in the northwest from the Cairngorm and South Grampians suite plutons in the southeast; he referred to this inferred structure as the Mid Grampian Line (MGL) (Fig. 2).

#### **4. Aims and objectives of this study**

Recent micro-analytical studies of zircons from granitoid rocks integrating oxygen, U-Pb, Hf isotope, and trace element/REE data (e.g. Kemp et al., 2007) have made significant advances in our understanding of the complex origin and evolution of granite suites, and their relationship to crustal growth. In addition, the ultra-high precision geochronological studies of zircon from granite plutons of (e.g.) the Sierra Nevada in California (Tuolumne Intrusive Suite, Coleman et al., 2004) and the Cretaceous North Cascades in Washington State (Mount Stuart batholith, Matzel et al., 2006) have provided important insights into pluton assembly and emplacement mechanisms.

However, to date only a limited number of such studies have been carried out and many uncertainties remain. Some aspects of pluton assembly and emplacement mechanisms have been largely resolved by ultra-high precision geochronology, but they provide no information about granite sources, genesis or magmatic processes that may have occurred during ascent and at shallower levels.

The aims and objectives of *this* study were to use an in-situ and integrated micro-analytical study of isotopic and trace element/REE signatures in zircons from the Scottish Caledonian granites to:

- Constrain the relative contributions to I-type granites made by contemporaneous mantle melts and recycled lower continental crust, and hence to quantify their contribution to Phanerozoic continental growth.
- Test previous and recent models of magma generation, ascent and emplacement.
- Identify open-system processes such as magma mixing, assimilation and hydrothermal alteration.
- Evaluate the scales of heterogeneity, and hence the complexity of plutonic magma systems, by combining information obtained on pluton-, sample-, crystal- and intra-crystal scales.
- Assess the applicability - and identify the limitations - of integrated multi-isotope and trace element studies of zircon to answering the above questions.
- Resolve the compositions and ages of the sources of Caledonian granite suites in more detail, explaining their observed whole-rock geochemical differences, and test existing models of the nature, ages and origins of the basement underlying the Grampian terrane.

To achieve these aims, several plutons from the classic late Caledonian granites were chosen for more detailed study. Like the LFB granites, the Caledonian granites have been studied for decades and an extensive data base of field, petrographic, whole-rock geochemical and isotopic data exists. Nevertheless, their origin, sources and petrogenetic histories remain largely unresolved. Thus, they represent an ideal location to use such an integrated approach, and to test existing regional and global models on the origin and evolution of granites.

For this purpose two I-type granites (Lochnagar and Etive) were selected (Fig. 2). The reasons for choosing these two plutons were that both are relatively well exposed, and have previously been mapped and studied in detail, providing a large data set of field relationships, petrographic descriptions, whole-rock and mineral chemical and isotopic data; these provide the basis for this integrated micro-

analytical study. In addition, based on the existing data the selected plutons differ in their complexity. The Lochnagar pluton represents a relatively simple composite pluton, comprising two main granite facies (L1 and L2), a third, locally developed, granite facies (L3), microgranites and several marginal diorites (Smith et al., 2001). In contrast, the Etive pluton comprises four main intrusive phases (the Meall Odhar, Cruachan, Starav and Quarry intrusions), which range in composition from granite to monzodiorite/diorite (Clayburn et al., 1983). Whole-rock geochemical and isotopic evidence suggests that both the Cruachan and Starav intrusions were emplaced in multiple pulses, and that the Starav Intrusion sourced different material than the other phases (Batchelor, 1987; Clayburn et al., 1983). Furthermore, based on differing whole-rock geochemical and isotopic compositions, the Lochnagar and Etive plutons are interpreted to belong to different granite suites – the Cairngorm and Argyll suites (Stephens and Halliday, 1984). To date the origin of these compositional differences is largely unresolved, but it has been suggested that they either reflect variations in the relative contributions of mantle and crust or differences in the nature of the underlying lower crustal and mantle reservoirs (Halliday, 1984).

In addition to the I-type granites, samples of three S-type granites (Kemnay, Cove and Nigg Bay) (Fig. 2) were collected. As previous studies suggest the S-type granites formed by melting of their current Dalradian Supergroup country rocks they are thought to have simple petrogenetic histories, which is in contrast to the late Caledonian I-type granites. The Kemnay, Cove and Nigg Bay granites are hosted by the same lithological unit of the Dalradian Supergroup, the Aberdeen Formation, hence probably have similar source rocks. However, they vary significantly in size (Kemnay: c. 36 km<sup>2</sup>, Cove: c. 1.7 km<sup>2</sup>, Nigg Bay: exact size unknown, but probably considerably smaller than Cove). The Dalradian Supergroup also comprises the host rocks to the I-type granites, and thus the S-type granites provide an important constraint on the types of crustal melts that might have contributed to the formation of the Lochnagar and Etive I-type plutons.

The main focus of this PhD study has been on zircons from the late Caledonian I-type granites as they have previously caused the most debate. As little or no work has been published to date on the S-type granites, this part of the project was considered a pilot study.

## 5. Methods

Recent developments in micro-analytical techniques enable analyses of oxygen, U-Pb isotopes, and trace and rare earth elements by ion microprobe (SIMS) and Hf isotopes by laser ablation-multi-collector ICP-MS (LA-MC-ICPMS) at high spatial resolution and precision in-situ in zircon. Due to the high spatial resolution of ion microprobe and laser ablation systems (~20  $\mu\text{m}$  and ~50  $\mu\text{m}$  respectively) multiple analyses may be made on a single zircon crystal (e.g. core and rim) enabling correlation of multiple isotopic and trace element data sets with textural information obtained from cathodoluminescence (CL) and backscattered electron (BSE) images, thereby providing access to otherwise inaccessible intra-grain variation. Furthermore, as in-situ analysis by SIMS consumes only very small amounts of sample material isotopes and trace elements may be measured in exactly the same area within each crystal, which permits direct correlation of the different data sets. The following sections give a background to the techniques employed in this study, including the utility of zircon as a petrogenetic indicator, and the applicability of isotopic and trace element/REE information stored in zircon to achieving the aims and objectives of this study.

### 5.1. Zircon

Zircon ( $\text{ZrSiO}_4$ ) is a common accessory mineral in igneous rocks of intermediate to silicic composition (Hoskin and Schaltegger, 2003). As it is chemically and mechanically extremely robust, it is able to preserve compositional information about the melt it crystallised from. Due to its refractory nature, crystals of zircon in igneous rocks commonly contain pre-magmatic ‘inherited’ cores (Fig. 3a) that are either inherited from the source region or assimilated from country rocks. Since the 1950s empirical and experimental studies have aimed to establish the temperatures and conditions under which zircon crystallises (e.g. Baker et al., 2002; Dickinson and Hess, 1982; Harrison et al., 2007; Keppler, 1993; Linnen and Keppler, 2002; Poldervaart, 1955, 1956; Watson, 1979, 1996b; Watson et al., 2006; Watson and Harrison, 1983, 2005). For the system  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Na}_2\text{O-K}_2\text{O}$  Watson (1979)

demonstrated that the Zr saturation level required for zircon to crystallise strongly depends on a melt's molar proportions of  $(\text{Na}_2\text{O}+\text{K}_2\text{O})/\text{Al}_2\text{O}_3$ , but only little on temperature,  $\text{SiO}_2$  content or  $\text{Na}_2\text{O}/\text{K}_2\text{O}$ . He also showed that in peraluminous melts less than 100 ppm Zr is needed to saturate the melt and crystallise zircon, which suggests that zirconium saturation is commonly reached early in their magmatic evolution (Corfu et al., 2003). Hence, zircon is likely to record information about the melt's primary composition and also any subsequent changes in melt composition, temperature or crystallisation conditions arising from either local closed-system processes or large-scale open-system changes (e.g. magma mixing, assimilation) (Hoskin and Schaltegger, 2003; Shore and Fowler, 1996; Vavra, 1990, 1993, 1994).

Igneous zircons typically vary in size between 20  $\mu\text{m}$  and 250  $\mu\text{m}$ , and are sub- or euhedral with a range of external morphologies (Hoskin and Schaltegger, 2003). Since the 1950s studies have attempted to use zircon morphologies as petrogenetic indicators (Hoffmann, 1981; Kostov, 1973; Larsen and Poldervaart, 1957; Poldervaart, 1955, 1956; Pupin and Turco, 1972a, b, c); the most widely used classification scheme was published by Pupin (1980). More recently it has been demonstrated that external zircon morphologies are of very limited use as petrogenetic indicators because zircons from a single rock and age population are often highly variable in their morphologies, those from different rock types may have similar morphologies, and the morphologies of zircon crystals commonly change during growth due to local kinetic factors such as diffusion rates and adsorption (Dowty, 1980; Vavra, 1990, 1993).

Zircons can incorporate large amounts of trace elements, such as Hf, Y, REE, P, U and Th (ppm to percent level) (Kinny and Maas, 2003), which are substituted into the crystal lattice either by simple (e.g.  $\text{U}^{4+} = \text{Zr}^{4+}$ ) (Fron del, 1953) or coupled (e.g.  $(\text{Y, REE})^{3+} + \text{P}^{5+} = \text{Zr}^{4+} + \text{Si}^{4+}$  = 'xenotime substitution') substitution (Speer, 1982). Intra-grain variations in Hf, P, Y, REEs, U and Th typically result in the development of oscillatory growth zoning (Fig. 3b), which is a common feature of magmatic zircon (e.g. Benisek and Finger, 1993; Fowler et al., 2002; Hanchar and Rudnick, 1995; Köppel and Sommerauer, 1974). Quite commonly growth zoning is interrupted by resorption surfaces, which reflect periods of Zr undersaturation in the

magma caused by either large-scale mixing events or local kinetic phenomena (Corfu et al., 2003).

In the past, zircons have been widely used for U-Th-Pb geochronology. However, they are also commonly used in trace element studies, in both igneous and metamorphic petrology. As recent developments in micro-analysis now allow measurement of oxygen and Hf isotopes at high spatial resolution and precision in-situ in zircon, they have become increasingly important in studies of crustal growth and evolution (e.g. Hawkesworth and Kemp, 2006a, b; Kemp et al., 2005, 2006, 2007).

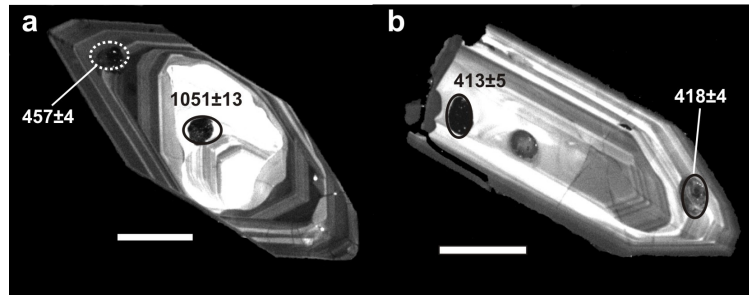


Fig. 3: CL images of (a) a zircon comprising an old inherited core (Kemnay Granite, grain 23) and (b) a magmatic zircon grown from the granite melt (L2 (Lochnagar pluton), grain 11).

## 5.2. Oxygen isotopes

The fractionation of oxygen isotopes between coexisting phases increases with decreasing temperatures, with Si-rich phases being enriched in  $^{18}\text{O}$  relative to Fe-rich and Si-poor phases. This contributes to the characteristic enrichment of  $^{18}\text{O}$  in crustal rocks relative to that of the Earth's mantle (Fig. 4). Thus, oxygen isotopes have been widely used in petrogenetic evolution studies of granitic rocks to constrain the relative contributions of mantle and crust. However, as the oxygen isotope compositions of granites and their constituent minerals are sensitive to modification by assimilation of  $^{18}\text{O}$ -enriched crustal rocks, magma mixing and hydrothermal alteration by  $^{18}\text{O}$ -depleted and/or  $^{18}\text{O}$ -enriched fluids (e.g. King et al., 1997, 2000; Monani and Valley, 2001; Valley and Graham, 1996), whole-rock studies often deliver ambiguous or controversial results.

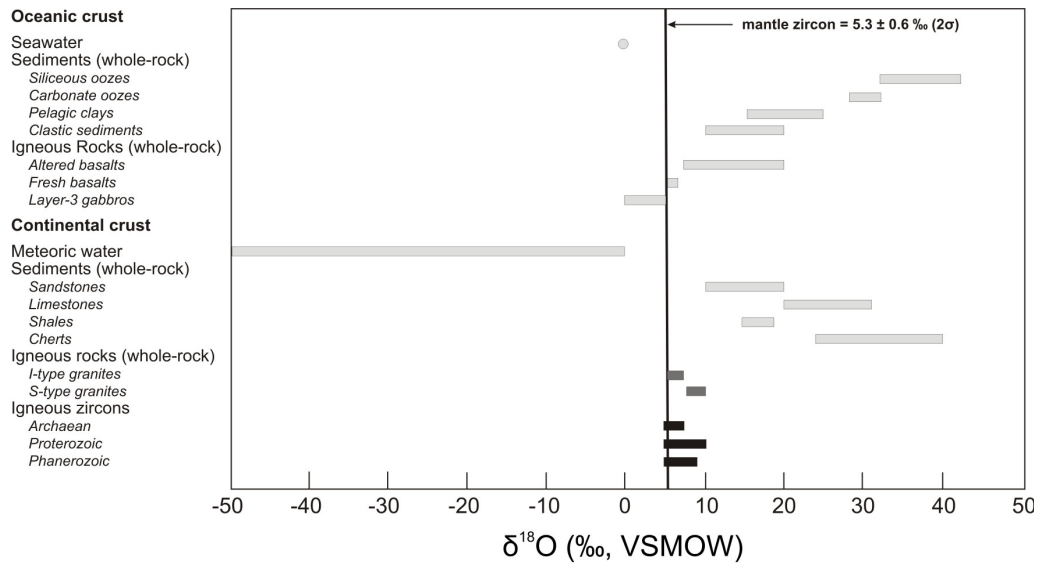


Fig. 4: Typical oxygen isotope compositions of sediments, igneous rocks and igneous zircons (modified from Eiler (2001) and Valley et al. (2005)).

Previous studies have shown that zircons preserve their  $\delta^{18}\text{O}$  values from the time of crystallisation due to very slow oxygen diffusion rates and high closure temperatures in comparison to most other minerals (Dodson, 1973; Page et al., 2007; Peck et al., 2003; Valley, 2003; Watson and Cherniak, 1997). Furthermore, zircon oxygen isotopes have been found to be insensitive to fractional crystallisation. In a closed system where all minerals are in isotopic equilibrium, whole-rock  $\delta^{18}\text{O}$  and the melt-zircon equilibrium fractionation factor ( $\Delta(\text{melt-Zrc})$ ) increase in parallel as differentiation and accompanying increase of  $\text{SiO}_2$  proceed (Valley et al., 1994). Thus, zircons may show mantle-like  $\delta^{18}\text{O}$  values of  $5.3 \pm 0.6$  ‰ ( $2\sigma$ ) (Valley et al., 1998), even if the host rock has a more evolved oxygen isotope composition due to differentiation. This makes oxygen isotope analysis of zircon a powerful tool to discriminate crustal and mantle sources.

Oxygen isotope analysis of zircon may also be used to investigate magmatic processes such as magma mixing, assimilation or hydrothermal alteration (Valley, 2003). As a change in  $\delta^{18}\text{O}$  (zircon) can only be achieved by adding material of differing oxygen isotope composition, an increase or decrease in  $\delta^{18}\text{O}$  with zircon growth can be considered evidence of open-system processes such as magma mixing or assimilation of crustal material (Valley, 2003). Contamination or assimilation that

occurs at a later stage in magma evolution can be evaluated by examining the state of isotopic equilibrium between zircon, which commonly precipitates early in the crystallisation sequence, and a mineral like quartz, which typically crystallises in the later stages (e.g. Bindeman and Valley, 2001; Criss and Taylor, 1986; Monani and Valley, 2001; Valley et al., 1994). Furthermore, by comparing the oxygen isotope compositions of zircon, quartz and their host rock it is possible to identify post-crystallisation hydrothermal alteration, which usually causes a change in  $\delta^{18}\text{O}$  of the whole-rock but not of zircon or quartz.

### *5.3. U-Pb dating*

The U-Th-Pb dating method is based on the radioactive decay of U and Th to stable isotopes of Pb, and has been used to date zircons since the 1950s (e.g. Larsen et al., 1952). Zircon is particularly suitable for U-Pb dating as it is chemically and mechanically extremely robust and readily incorporates U and Th. However, due to the large difference in ionic radii substitution does not occur between Zr and Pb. Thus, in principle all measured Pb stems from the radioactive decay of U and Th, and by determining the concentrations of U, Th and Pb and the isotopic composition of Pb the crystallisation age of the zircon crystal can be calculated (Faure and Mensing, 2004). Due to the precision of  $\sim 1\%$  of SIMS U-Pb analysis this age is considered to represent the most reliable estimate of the timing of pluton crystallisation in older granitoid rocks. However, on young ( $115 \pm 3$  ka) rhyolite lavas from the Long Valley Caldera, California it has been demonstrated that zircons can remain suspended for long periods ( $> 100$  ka) in the convecting portions of a magma (Reid et al., 1997). Here crystallisation ages represent the time at which the zircon saturation temperature was reached in the magma, which in the case of the Long Valley rhyolite lavas occurred approximately 100 ka prior to eruption. Recently, U-Pb dating has also become a very important tool in identifying differences in ages between individual melt batches, which led to the model of incremental assembly (e.g. Coleman et al., 2004). In addition, U-Pb dating can also provide critical evidence of the age of magma source rocks, as igneous rocks commonly contain older zircon



cores which were either inherited from the source region or by late-stage assimilation of a supracrustal component (Corfu et al., 2003; Pidgeon and Aftalion, 1978).

#### *5.4. Trace elements/REEs*

Zircon is known to incorporate up to 25 different elements, the most abundant being Hf, Y, REEs, P, U and Th, which are incorporated into the crystal lattice by simple or coupled substitutions. Normalised against chondrite, crustal zircons typically show REE patterns with slopes rising steeply from the LREE to the HREE, a positive Ce anomaly ( $Ce/Ce^*$ ) and a negative Eu anomaly ( $Eu/Eu^*$ ), which is a result of differences in compatibility (Hoskin and Schaltegger, 2003).

The ability of zircon to record and retain information about its parental melt inspired several authors to assess the applicability of trace element/REE concentrations and variations to petrogenesis and provenance-indicator studies (Belousova et al., 2002; Heaman et al., 1990; Hoskin and Ireland, 2000). These studies showed that crustal zircons from rocks ranging in composition from mafic to felsic have generally similar REE patterns. In addition, REE abundances in zircon commonly vary at an inter- and intra-grain scale (between c. 250 ppm to 5000 ppm) (e.g. Black et al., 1986). The processes that control the incorporation of trace elements and REEs into zircon are not well constrained, and little is known about how much the zircon chemistry is affected by crystallisation conditions and the overall growth environment (e.g. Guo et al., 1996; Hinton and Upton, 1991). These factors led to the conclusion that the REE chemistry of zircons is of limited use as a petrogenetic tool (Hoskin and Schaltegger, 2003). However, it was also shown that mantle zircons lack significant Eu anomalies and have flatter HREE patterns, hence are distinctly different from crustal zircons. These differences may be used to discriminate between rocks with mantle affinities and those with crustal affinities (Belousova et al., 1998; Heaman et al., 1990; Hoskin, 1998; Hoskin and Ireland, 2000).

### 5.5. Hf isotopes

Like the Sm-Nd system, the Lu-Hf isotopic system can be used to decipher the differentiation history of the Earth's mantle and crust. During mantle melting  $^{176}\text{Hf}$ , the stable decay product of  $^{176}\text{Lu}$ , is more incompatible than Lu, which leads to depletion in Hf of the residual mantle and enrichment in the crust (Patchett et al., 1981) (Fig. 5). Thus, the generation of basaltic magmas has caused the originally uniform and approximately chondritic initial Lu/Hf ratio of the Bulk Silicate Earth (or Chondritic Universal Reservoir = CHUR) to be progressively modified, resulting in a Lu/Hf ratio higher than CHUR in the depleted mantle and lower than CHUR in the enriched crust (Kinny and Maas, 2003).

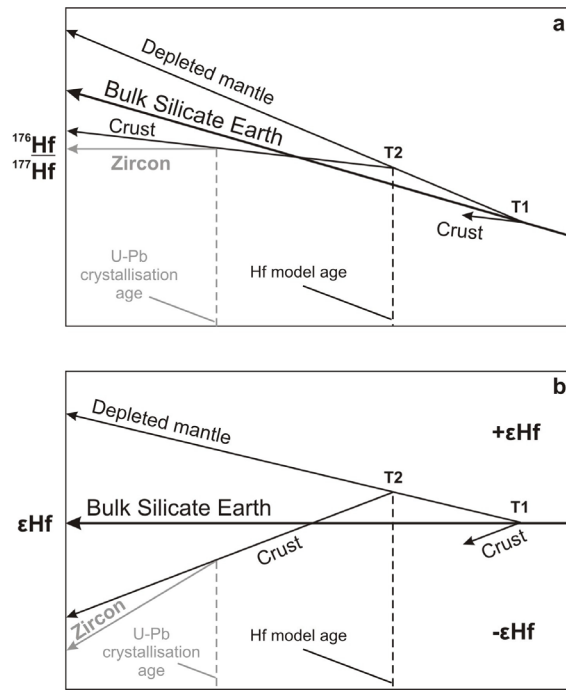


Fig. 5: Evolution of the Bulk Silicate Earth, depleted mantle and continental crust (see text). T1 and T2 represent two melting events (modified from Scherer et al., 2007).

Since Hf isotopes may now be measured at relatively high spatial resolution and precision in-situ in zircon they have become an essential tool in crustal evolution studies. Zircon is particularly suitable for Hf isotope analysis as most zircon crystals contain 0.5-2.0 wt%  $\text{Hf}_2\text{O}$  (Hoskin and Schaltegger, 2003). In addition, as the  $^{176}\text{Lu}/^{177}\text{Hf}$  ratio of zircon is usually  $< 0.0005$ , in-situ decay of  $^{176}\text{Lu}$  in the zircon crystal typically has a negligible effect. Hence, zircons preserve close to their initial

$^{176}\text{Hf}/^{177}\text{Hf}$  ratio and that of their parent magma from their time of crystallisation. This ratio may be used to determine  $\epsilon\text{Hf}$  values (deviations in Hf isotopic composition from CHUR in parts per ten thousand) and to calculate Hf model ages, i.e. the approximate time at which the protolith separated from the depleted mantle (Kinny and Maas, 2003). Thus, in the study of granites, Hf isotopes of zircons provide valuable information on the compositions and ages of granite sources, especially when used in combination with oxygen and U-Pb isotope data. These may be used to constrain the presence and proportion of pristine mantle material in the zircons, and hence a granite's contribution to continental growth. The Hf model ages may be compared with the crystallisation ages of granites determined by U-Pb dating; if the model ages are much older than the crystallisation ages, the contribution of contemporaneous juvenile mantle melts may be discounted.

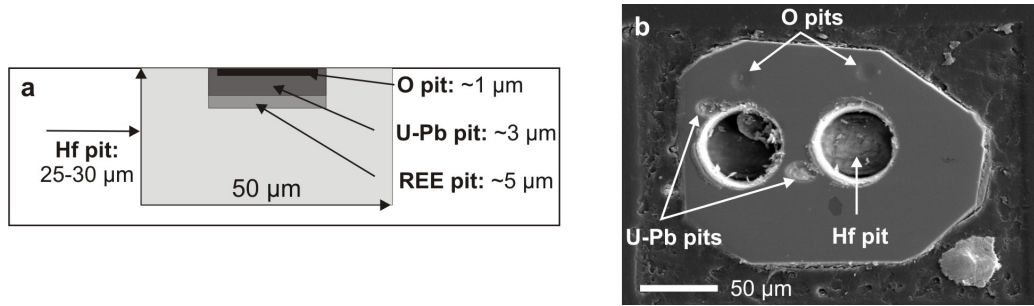


Fig. 6: (a) Sketch of pit sizes of SIMS oxygen, U-Pb isotope and trace element/REE analyses, and of laser ablation ICPMS Hf isotope analysis; (b) Secondary Electron image of zircon crystal with oxygen, U-Pb and Hf isotope pits.

### 5.6. Analytical protocols

As each type of analysis consumes different amounts of material, with oxygen isotope analysis consuming the least and Hf isotope analysis the most, analyses must be carried out in a particular order with oxygen isotopes measured first and Hf isotopes last (Fig. 6). Furthermore, oxygen isotope analysis by SIMS is very sensitive to surface irregularities, and may be affected by topography created by previous analyses. In addition, oxygen flooding of the sample surface is employed during U-Pb analysis to enhance Pb ion yields, which may lead to abnormal  $\delta^{18}\text{O}$  values. Assuming the zircon does not contain older components, this order of analysis can be

reversed, but only if the sample surface is re-polished and an undisturbed layer of the crystal exposed prior to oxygen isotope analysis.

Prior to analysis approximately 100 zircons per sample were hand-picked and mounted into epoxy, and subsequently imaged under transmitted and reflected light, and using CL and BSE imaging techniques. For oxygen isotope analysis, which produces the smallest and shallowest ion probe pits (~18  $\mu\text{m}$  across and ~1  $\mu\text{m}$  deep) (Fig. 6), between 20 and 30 ideally clear, crack- and inclusion-free zircons per sample were selected. Zircons were selected for analysis if they were considered to be representative with respect to grain size, morphology and internal zoning. To enable detection of changes in oxygen isotope composition with zircon growth multiple analyses were typically made on a single zircon crystal. However, due to the poor grain quality in some samples this was not always possible. Analyses of U-Pb isotopes and trace elements/REEs, which generate slightly larger pits (~25  $\mu\text{m}$  across and ~3-5  $\mu\text{m}$  deep) (Fig. 6), were carried out next. Due to much longer data acquisition times (O: c. 3.5 minutes, U-Pb and trace elements/REEs: c. 30 minutes) U-Pb isotope, trace element and REE data were obtained on only a sub-set (between 10 and 15 zircons per sample) of crystals. Commonly, analyses were made in the same area or at least within the same CL zone as the oxygen isotope analysis. Because analysis by LA-MC-ICPMS consumes a much larger amount of sample material than ion microprobe analysis, typically ablation pits that are 50  $\mu\text{m}$  across and ~25-30  $\mu\text{m}$  deep (Fig. 6), Hf isotopes were analysed last. Generally, the aim was to obtain Hf isotope data from zircon crystals and areas within the crystal for which U-Pb and oxygen isotope data already existed. However, this objective was greatly limited by the much larger size of the laser beam, and resulted in a much smaller data set. Thus, some analyses were also made on crystals for which either no oxygen or no U-Pb data existed. Nevertheless, outermost zircon rims were often too narrow to analyse by laser ablation and are therefore generally under-represented in the data set.

Subsequent to analysis, zircons were again imaged by CL and BSE to determine the exact position of each analysis, and to check for inclusions and cracks in the bottom of each pit. Data from dubious locations were rejected. Further data were rejected from zircons showing high concentrations of common Pb, discordance (U-

Pb: > 10 %, O: > 20 % discordance), and more than 1000 ppm U. This resulted in a considerably smaller, but very robust, data set.

## **6. Thesis layout**

This PhD thesis comprises four papers. Papers 1 to 3 focus on the genesis of the late Caledonian I-type granites, and paper 4 on the S-type granites.

The first zircon oxygen isotope data obtained in this PhD project showed that the Lochnagar pluton comprises homogeneous and heterogeneous samples. The objective of Paper 1 was to investigate this in more detail by comparing the zircon, quartz and whole-rock oxygen isotope data of two representative samples, one homogeneous in zircon  $\delta^{18}\text{O}$  (Cul nan Gad diorite) and one heterogeneous (Allt Darrarie diorite). By combining the different data sets it was possible to study the petrogenetic histories from genesis to post-crystallisation hydrothermal alteration of both samples. Paper 2 presents oxygen, U-Pb isotope and trace element/REE data of zircons from the remaining Lochnagar samples and of the Etive samples in order to constrain their emplacement histories, and to assess the role of mantle, infracrustal and supracrustal sources in their genesis. One major outcome of this part of the study was that the  $\delta^{18}\text{O}$  (zircon) data of the Lochnagar and Etive plutons are very similar, hence fail to explain the whole-rock differences between the plutons. The zircon oxygen isotope data also revealed that both plutons appear to contain only a small proportion of zircons with mantle-like  $\delta^{18}\text{O}$  values. However, from these data alone it was not possible to investigate whether these mantle-like zircons represent involvement of contemporary (~420 Ma) mantle-derived material, thus indicate crustal growth, or represent melting of mafic lower crust, thus crustal recycling. To resolve this, and to explain the whole-rock geochemical differences between the plutons Paper 3 integrates the zircon oxygen isotope data presented in Paper 2 with zircon Hf isotope data. The aim of Paper 4 was to determine the crystallisation ages (which had previously not been determined) and sources of the Kemnay, Cove and Nigg Bay S-type granites by integrating oxygen, U-Pb and Hf isotope data of

zircon. The following sections give a more detailed summary of the objectives, results and conclusions of each paper.

*Paper 1: A cryptic record of magma mixing in diorites revealed by high-precision SIMS oxygen isotope analysis of zircons*

The combination of oxygen isotope data for zircon, quartz and whole-rock in granitic rocks has been shown to provide detailed insights into the petrogenetic and post-crystallisation alteration history of plutons (e.g. King et al., 1997; King and Valley, 2001; Monani and Valley, 2001). Previous studies have assessed the state of equilibrium between zircon, quartz and whole-rock based on conventional laser fluorination data (King et al., 1997, 1998, 2001, 2004; Lackey et al., 2005, 2006; Monani and Valley, 2001). However, this paper presents high-precision in-situ ion microprobe oxygen isotope analyses of zircon and quartz, supported by whole-rock oxygen isotope data, for two diorite intrusions forming part of the late Caledonian Lochnagar pluton.

The Allt Darrarie (AD) and Cul nan Gad (CnG) diorites form two small intrusions (areal dimensions of 0.6 x 0.4 km and 4-5 x 1.8 km, respectively) along the margin of the Lochnagar pluton. Based on petrographic and field data they have been interpreted to be related to, but older than, the Lochnagar pluton (Smith et al., 2001). However, new U-Pb SIMS dating of the diorites shows that they were emplaced contemporaneously with and subsequent to the main granite body (Paper 2). Compositionally and texturally the diorites are very similar; both are dark grey, fine- to medium-grained, and comprise plagioclase (45-50 %), biotite (c. 40 %), hornblende (< 5-10 %) and interstitial quartz (c. 5 %), with accessory ilmenite and magnetite, titanite (absent in CnG), zircon and apatite. Evidence of restitic or cumulate material was not found in either sample.

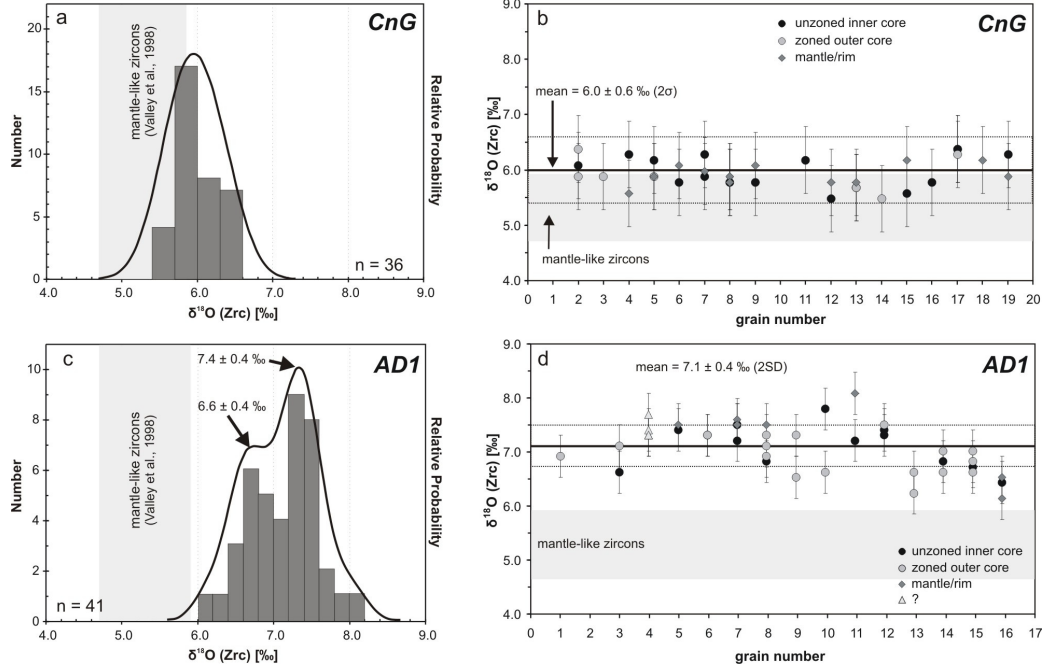


Fig. 7: Cumulative probability-histograms and grain-scale variation plot of zircon crystals from the Cul nan Gad (a & b) and Allt Darrarie diorites (c & d).  
a) CnG zircons show a narrow range in  $\delta^{18}\text{O}$  values and a single mode (bin widths of histograms equal  $1\sigma$ , error bars are  $2\sigma$ ).  
b) All data from the CnG zircons lie within 2 of the mean (dotted area).  
c) AD1 zircons display a much larger range than CnG zircons and an apparent bimodal distribution (bin widths of histograms equal  $1\sigma$ , error bars are  $2\sigma$ ).  
d) Data are more scattered and not all lie within error of the mean. Prominent inter-grain variation in  $\delta^{18}\text{O}$  occurs between e.g. grains 7 and 16, intra-grain variation between inner and outer core (grain 9), core and rim (grain 11).  $\delta^{18}\text{O}$  commonly increases with zircon growth except in grain 10.

Despite these similarities, oxygen isotope analyses of zircons from the Allt Darrarie and Cul nan Gad diorites reveal large differences in the degree of heterogeneity, data distribution and mean  $\delta^{18}\text{O}$  compositions (Fig. 7). Zircon crystals from the Cul nan Gad diorite show a unimodal distribution of oxygen isotope values ( $\delta^{18}\text{O} = 6.0 \pm 0.6 \text{‰}$  ( $2\sigma$ ,  $n=36$ )) with a standard deviation comparable to that of the homogeneous analytical zircon standard, and no - or only minor - intra-grain variation. In contrast, those from the Allt Darrarie diorite display a large range in  $\delta^{18}\text{O}$ , an apparent bimodal distribution with modes of  $6.6 \pm 0.4 \text{‰}$  and  $7.3 \pm 0.4 \text{‰}$  ( $n=41$ ), and inter- and intra-grain variations of up to  $1.2 \text{‰}$ . Where intra-grain variations were detected both an increase and decrease in  $\delta^{18}\text{O}$  with zircon growth was observed. As the  $\delta^{18}\text{O}$  composition of growing zircon can only evolve by open-system changes to the magma composition, i.e. if material of contrasting  $\delta^{18}\text{O}$

composition is added to the magma, the intra-grain variation in zircons of the Allt Darrarie diorite is interpreted to represent a cryptic record of magma mixing of which no other evidence was found in the sample. As simple mixing with a supracrustal component would result in an increase in  $\delta^{18}\text{O}$ , but never a decrease, the Allt Darrarie magma must have had a more complicated mixing history.

Recently, it has been proposed that ‘deep crustal hot zones’, which result from repeated intrusion of mantle-derived basalt sills into the lower crust, are a likely site for formation of intermediate and silicic magmas. Magmas are either produced by differentiation of basaltic sills, mixing of residual melts and crustal partial melts or by melting of lower crustal rocks, which creates a large range of intermediate and silicic melts of varying oxygen isotope composition (Annen et al., 2006). Based on the large inter- and intra-grain variations in  $\delta^{18}\text{O}$  (zircon) in the Allt Darrarie diorite, generation in a deep crustal hot zone appears possible. Mantle-derived zircon has a  $\delta^{18}\text{O}$  value of  $5.3 \pm 0.6 \text{ ‰}$  ( $2\sigma$ , Valley et al., 1998). The  $\delta^{18}\text{O}$  range of zircon from the Allt Darrarie diorite is 6.1-8.1 ‰, hence none of the zircon in this intrusion has a mantle-like composition. By contrast, a  $\delta^{18}\text{O}$  range of 5.5-6.4 ‰ for zircon from the Cul nan Gad diorite includes a number of analyses with mantle-like values. From oxygen isotope data alone it is not possible to decipher whether the diorites represent a mixture of mantle-derived and crustal material or were generated by recycling of infra- and supracrustal sources.

In contrast to the zircon data, the quartz oxygen isotope data from the Cul nan Gad and Allt Darrarie diorites display only minor variation (CnG:  $10.9 \pm 0.5 \text{ ‰}$  ( $2\sigma$ ,  $n=22$ ), AD1:  $11.7 \pm 0.6 \text{ ‰}$  ( $2\sigma$ ,  $n=27$ )) within each sample, with no evidence of mixing. As quartz and zircon display isotopic disequilibrium (Fig. 8) in both diorites quartz probably crystallised later in the crystallisation sequence; in the Allt Darrarie diorite it precipitated after the inferred magma mixing from a homogenised, higher  $\delta^{18}\text{O}$  melt.



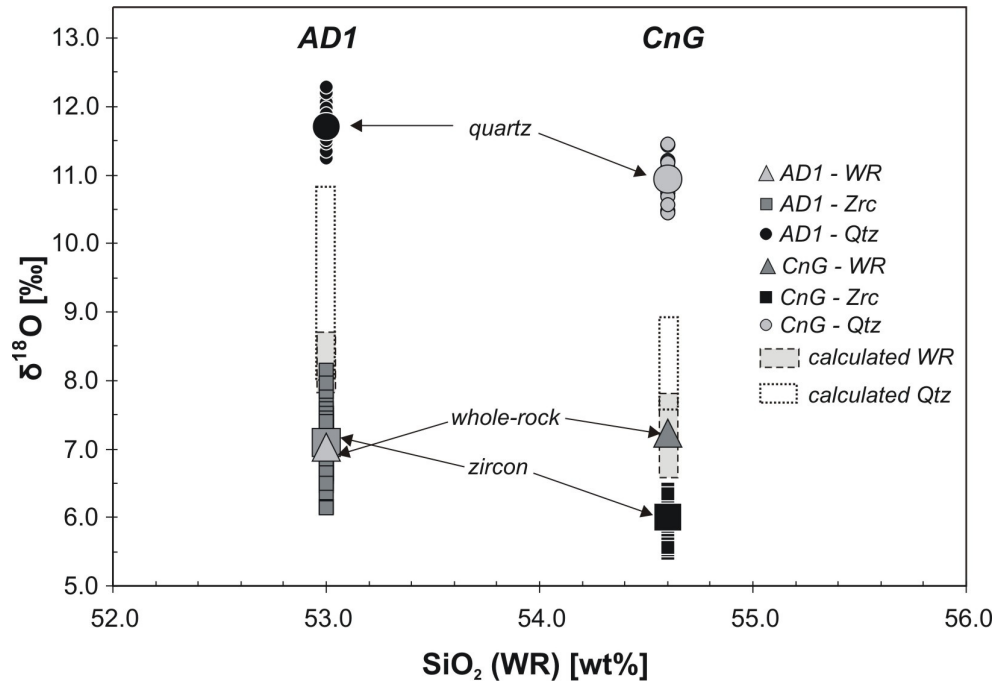


Fig. 8: Evaluation of equilibrium between zircon (Zrc), quartz (Qtz) and whole-rock (WR). 'Calculated WR' and 'calculated quartz' are calculated using equations (1) and (2) (see text); calculations include the error on the zircon analysis.

AD1: Zircon is not in equilibrium with quartz or whole-rock. Measured whole-rock is too low to be in equilibrium with zircon, which suggests it was affected by hydrothermal alteration after zircon crystallisation.

CnG: Zircon and quartz are not in equilibrium as measured quartz  $\delta^{18}\text{O}$  is considerably higher than the calculated quartz value, which suggests quartz crystallised late in sequence. Zircon and whole-rock are in equilibrium. Low modal percentage of elevated quartz in whole-rock (< 5 %) did not shift whole-rock out of equilibrium.

Comparison of whole-rock and zircon  $\delta^{18}\text{O}$  data shows them to be in equilibrium in the Cul nan Gad diorite, whereas in the Allt Darrarie diorite the whole-rock  $\delta^{18}\text{O}$  value is too low (Fig. 8) indicating that it probably experienced hydrothermal alteration that did not affect zircon or quartz.

This study shows that a combination of zircon, quartz and whole-rock data is a powerful tool to reconstruct the petrogenetic evolution of plutons from early crystallisation to late alteration. In addition, high-precision SIMS oxygen isotope analysis of zircon provides a new approach to identifying and resolving previously undetected early-stage magma mixing events and constraining the compositions and origins of the component magmas.

Based on their differing whole-rock geochemical compositions the Lochnagar and Etive plutons have been interpreted to belong to different granite suites – the Cairngorm and Argyll suites, respectively (Fig. 2). To date the reasons for these whole-rock differences are not resolved, but it has been proposed that they may reflect heterogeneities in the composition and age of the underlying lower crust and/or mantle, or differences in the relative contributions made by the crust and mantle (Halliday, 1984).

To resolve the sources and petrogenetic evolutions of the Lochnagar and Etive plutons oxygen isotope analyses together with U-Pb isotope and trace element/REE analyses were carried out on zircons from a suite of granite and diorite samples of both plutons.

Zircons from the Lochnagar and Etive plutons have the same mean  $\delta^{18}\text{O}$  values (Lochnagar:  $6.6 \pm 0.6$  ‰ ( $2\sigma$ ,  $n=230$ ); Etive:  $6.5 \pm 0.4$  ‰ ( $n=209$ ), and each pluton yielded a similar small proportion (c. 18 %) of analyses with mantle-like values ( $5.3 \pm 0.6$  ‰ ( $2\sigma$ , Valley et al., 1998)). This leads to two important conclusions: (1) The relative contributions of mantle and crust to magma genesis have probably been similar in both plutons, and therefore the whole-rock differences between them most likely reflect compositional differences between their lower crustal sources. Zircon trace element and REE data have been found to be overall similar in both plutons, and hence do not provide further information on the sources. (2) Based on the small proportion of mantle-like zircons, the Lochnagar and Etive plutons, and possibly the late Caledonian I-type granites as a whole, probably made some contribution to net crustal growth. However, from oxygen isotope data alone it is not clear whether the small proportion of zircon analyses with mantle-like values reflects sourcing of contemporary ~420 Ma mantle, and thus generation of new crust, or of ancient mafic material, e.g. a mafic underplate, and thus crustal recycling.

Samples from both plutons may be homogeneous or heterogeneous in terms of the distribution of  $\delta^{18}\text{O}$  values in zircon (Fig. 9). In heterogeneous samples, resolvable variations in  $\delta^{18}\text{O}$  occur between zircon crystals of a single sample and

even within individual zircons. This degree and scale of heterogeneity have not previously been reported. Where resolvable intra-grain variations were detected, both decreases and increases of  $\delta^{18}\text{O}$  with zircon growth were observed, providing evidence for magma mixing.

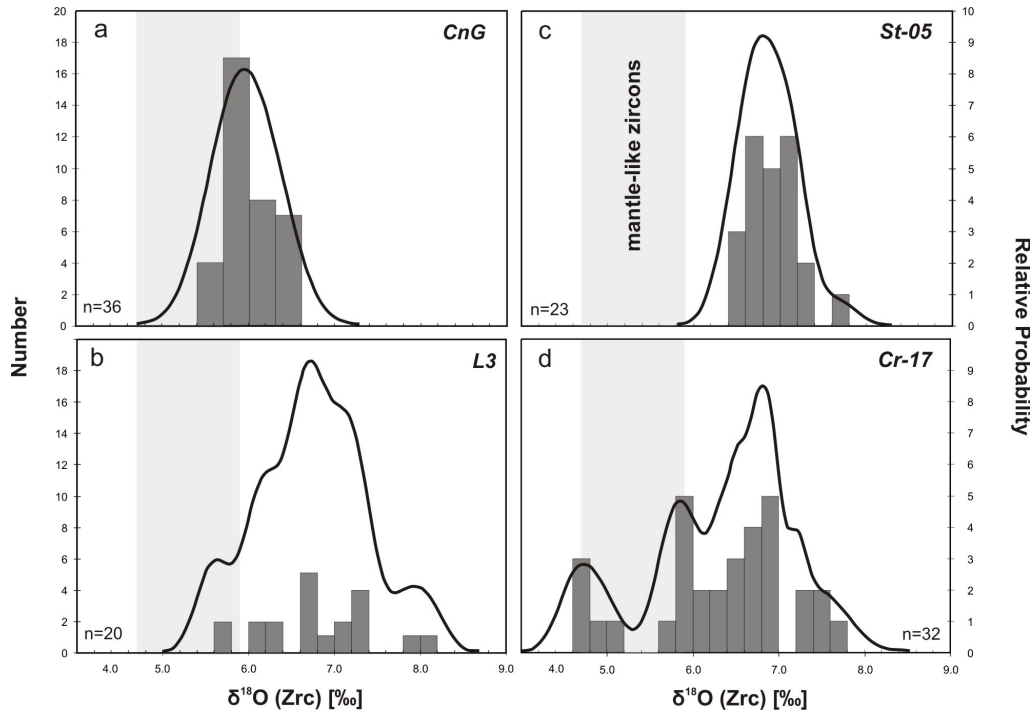


Fig. 9: Oxygen isotope probability-histograms of zircons from homogeneous and heterogeneous Lochnagar (a & b) and Etive (c & d) pluton samples. (CnG = Cul nan Gad diorite, St-05 = Starav Intrusion, Cr-17 = Cruachan Intrusion; bin width =  $1\sigma$ , probability curves were calculated at  $1\sigma$ ).

Evidence for the complex petrogenetic evolution and assembly of the plutons was also found in the U-Pb isotope data, which revealed that the emplacement histories of both plutons are more protracted and complicated than previously recognised, with magmatic activity at the Lochnagar pluton lasting for c. 11 m.y. ( $424 \pm 5$  Ma to  $413 \pm 4$  Ma) and at the Etive pluton for c. 16 m.y. ( $423 \pm 2$  Ma and  $407 \pm 2$  Ma).

The large variation in  $\delta^{18}\text{O}$  in zircons of the Allt Darrarie and Cul nan Gad diorites is attributed to magma generation in a ‘deep crustal hot zone’ (Annen et al., 2006) where mantle melts differentiated, inducing partial melting of the lower/middle crust and extensive mixing of melts with differing  $\delta^{18}\text{O}$ . Based on intra-grain variations in  $\delta^{18}\text{O}$  further mixing occurred during zircon growth during

ascent and at shallower levels. Magmas were subsequently emplaced incrementally in small batches over extended periods of time, consistent with the U-Pb data.

To summarise, even though the reasons for whole-rock geochemical differences between the Lochnagar and Etive plutons have not been fully resolved by this study, integrating  $\delta^{18}\text{O}$  and U-Pb isotope data is a powerful tool to constrain the petrogenesis of the plutons, their very complex evolution and the mechanisms of emplacement.

*Paper 3: Using in-situ O and Hf isotope analysis of zircons to constrain the sources of late Caledonian granites in Scotland*

Oxygen and U-Pb isotope analyses of zircons from the Lochnagar and Etive plutons gave some insight into the relative contributions made by crust and mantle, and furthermore deciphered important aspects of the plutons' genesis, evolution, emplacement mechanisms and histories. However, three questions could not be resolved: (1) Do the zircons with mantle-like  $\delta^{18}\text{O}$  values represent contemporary mantle (~420 Ma), thus generation of new crust, or melting of ancient mafic material in the lower crust (e.g. a mafic underplate), thus recycling of crust? (2) What caused the whole-rock compositional differences between the plutons? (3) What are the compositions and ages of the lower crustal sources that contributed to the plutons, and hence of the basement beneath the Grampian Highlands?

The integration of oxygen and Hf isotopes of zircons has been shown to be a powerful approach to constrain the amount of contemporary mantle melting, and the compositions and approximate ages of sources (e.g. Kemp et al., 2007). Thus, in order to resolve the above questions this integrated approach is applied here to zircons of the Lochnagar and Etive plutons.

Initial  $\epsilon\text{Hf}$  values of zircons from the Lochnagar pluton spread from +3.4 to -5.8  $\pm 1.0$  ( $2\sigma$ ) (=9.2  $\epsilon\text{Hf}$  units) (Fig. 10). The spread results from differences in  $\epsilon\text{Hf}$  between samples and between zircons of a single sample; where multiple analyses were made on a single zircon crystal from either pluton  $\epsilon\text{Hf}$  values are always within error. This variability supports the model of generation in a deep crustal hot zone and incremental assembly proposed in Papers 1 and 2. The majority of samples display

values between +2.7 and -2.8  $\epsilon_{\text{Hf}}$ , but two samples are clearly different. Zircons from one sample of L1 granite show only negative  $\epsilon_{\text{Hf}}$  values (-1.5 to -5.8) while those from a second sample of L1 granite display values between +1.2 and -2.3; zircons from the marginal Allt Darrarie diorite extend to even more negative values and are overall much more heterogeneous than the main data cluster (+3.4 to -4.8).

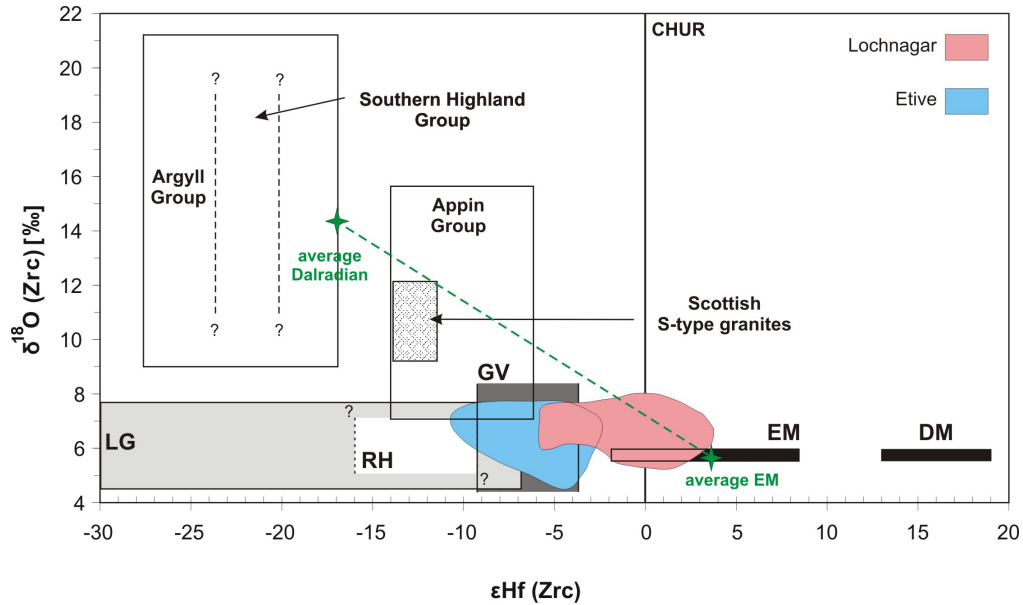


Fig. 10:  $\epsilon_{\text{Hf}}$  vs.  $\delta^{18}\text{O}$  of zircons from the Lochnagar and Etive plutons showing the relationship to their potential supracrustal and infracrustal sources. Zircons from both plutons show no overlap with the field defined by depleted mantle (DM, re-calculated at 420 Ma), but those from the Lochnagar pluton show strong overlap with enriched mantle (EM). The mixing line (green dashed line) reflects simple two-component mixing between EM and average Dalradian (i.e. Appin, Argyll and Southern Highland groups). Based on this mixing modelling both plutons may contain up to 30 % Dalradian material. However, the complexity and variation observed in the zircon oxygen isotope data indicates involvement of more than two sources. Large overlap exists with fields representing the plutons' potential lower crustal source rocks (i.e. Lewisian granulites = LG, Rhinn's Complex = RH, Grenville-age basement = GV). Hf isotope data (at 420 Ma) of potential sources were calculated based on published Nd isotope data (assuming a Hf-Nd correlation of the terrestrial array (Vervoort and Blichert-Toft, 1999)) by Anderson et al. (2004), Canning et al. (1998), Frost and O'Nions, (1985), Halliday (1984), Hamilton et al. (1980), Harmon (1983), Kay (1980), Muir et al. (1994), O'Nions et al. (1983), Restrepo-Pace et al. (1997), Thirlwall (1982).

Zircons from the Etive pluton show  $\epsilon_{\text{Hf}}$  values of  $-3.0$  to  $-10.6 \pm 1.0$  ( $2\sigma$ ) ( $=7.6$   $\epsilon_{\text{Hf}}$  units) (Fig. 10). In contrast to zircons from the Lochnagar pluton, they form two distinct data clusters. The first cluster ranges from  $-3.0$  to  $-7.3$   $\epsilon_{\text{Hf}}$  and comprises zircons from the Meall Odhar, Cruachan and Quarry intrusions; the second cluster is

represented by zircons from the Starav Intrusion and spreads between -8.3 and -10.6  $\epsilon\text{Hf}$ .

The  $\epsilon\text{Hf}$  data indicate that the Lochnagar and Etive plutons comprise material of at least two sources of different  $\epsilon\text{Hf}$ . With a data range of +3.4 to -5.8 for zircons from the Lochnagar pluton and -3.0 to -10.6 for zircons from the Etive pluton a significant contribution by contemporary depleted mantle, which had an  $\epsilon\text{Hf}$  value of approximately +16 (Vervoort and Blichert-Toft, 1999), can be precluded. Little is known about the composition of the mantle beneath the Grampian terrane. However,  $\epsilon\text{Nd}$  values for Old Red Sandstone lavas (Thirlwall, 1982) and for two lamprophyre suites (Canning et al., 1998) indicate that the mantle below Scotland is highly heterogeneous and at least locally enriched. Thus, for the Lochnagar pluton involvement of a small enriched mantle component may be possible, but much more negative  $\epsilon\text{Hf}$  values for the Etive pluton make it less likely here. Simple two-component magma mixing modelling between the two obvious end-members, i.e. enriched mantle and rocks of the Dalradian Supergroup shows that the Lochnagar pluton may comprise a large enriched mantle (70-100 %) component. However, the complexity and variation observed in the zircon oxygen isotope data indicates a much more complex mixing scenario involving more than two sources.

Variations in composition between the potential mafic components may in part be responsible for the whole-rock differences between the plutons. However, compositional differences between the unknown crustal sources will have also played an important role. This is supported by Hf model ages (calculated based on the  $^{176}\text{Lu}/^{177}\text{Hf}$  ratio of the average crust and on the  $^{176}\text{Lu}/^{177}\text{Hf}$  ratio of each whole-rock sample), which indicate that the Lochnagar pluton melted lower crustal material that separated from the mantle between approximately 1.7 Ga and 1.0 Ga, whereas the Etive pluton sourced material with Hf model ages between 2.1 Ga and 1.2 Ga (Fig. 11). As Hf model ages strongly depend on the  $^{176}\text{Lu}/^{177}\text{Hf}$  ratio used for the calculation, the above ages have to be considered as rough estimates. Nevertheless, they clearly show that the Etive pluton melted at least some older material, which supports the  $\epsilon\text{Hf}$  data and indicates that the basement beneath the pluton is different in part to that beneath the Lochnagar pluton.

Due to lack of outcrop, little is known about the basement beneath the Grampian Highlands. Based on geophysical constraints, geochemical and isotopic data for the late Caledonian granites, U-Pb ages of inherited zircons found in the granites and wider geological arguments, it has been proposed that rocks of the Lewisian Complex (c. 2.9 Ga), the Rhinns Complex (c. 1.8), Grenvillian basement (1.2-1.0 Ga), and of the Dava and Glen Banchor successions (i.e. gneisses, locally migmatised psammities, semi-pelites and subordinate quartzites that were derived from Palaeoproterozoic- and Grenville-age sedimentary protoliths) underlie the Grampian Highlands. However, due to the ambiguities of calculating Hf model ages these cannot be easily linked to the Hf model ages of the plutons. Thus, perhaps the most reasonable model for the lower crust beneath the Grampian terrane is that it comprises a range of Archaean- to Neoproterozoic-age material. The contributions from these sources vary between the plutons, with the Lochnagar pluton predominantly representing larger proportions of Mesoproterozoic-age, and the Etive pluton of Meso- and Palaeoproterozoic age lower crust.

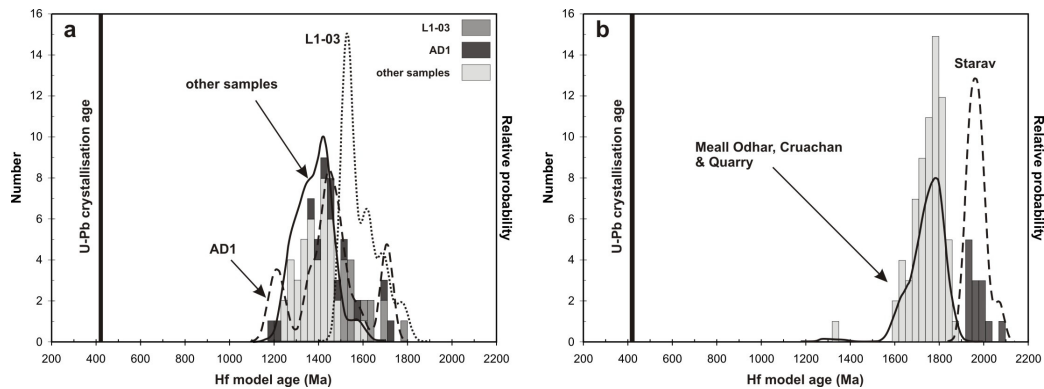


Fig. 11: Hf model ages ( $TDM_C$ ) of zircons from (a) the Lochnagar pluton and (b) the Etive pluton (probability curves were calculated at  $1\sigma$ , bin width =  $1\sigma$ ).

In summary, this study shows that the basement beneath the Grampian Highlands is variable in composition and age. This lends support to the hypothesis that the geochemical differences between the Lochnagar and Etive plutons, and on a wider scale between the Cairngorm and Argyll suites, lie dominantly in the differences in

the ages and compositions of their underlying lower crustal sources, and not in differences in the relative contributions made by crust and mantle.

*Paper 4: An integrated zircon O, U-Pb and Hf isotope study of zircons in S-type granites*

Previous studies have shown that most I-type granites comprise multiple sources and have complicated petrogenetic histories (e.g. Kemp et al., 2007; Papers 1 to 3). S-type granites are widely considered to typically comprise only a single supracrustal/sedimentary source and therefore provide the opportunity to study one of the end-members that commonly contribute to I-type granites.

Papers 1 to 3 showed that the origin and evolution of complex I-type granites may now be deciphered by integrated in-situ ion microprobe and laser ablation ICPMS oxygen, U-Pb and Hf isotope analyses of zircons. Thus, the same approach is applied here to zircons from the Scottish Caledonian Kemnay, Cove and Nigg Bay S-type granites in order to constrain their crystallisation ages (which had previously not been determined) and sources.

The Kemnay, Cove and Nigg Bay granites are all located in the northeastern Grampian Highlands, and crop out in the Aberdeen Formation of the Dalradian Supergroup (Stephenson and Gould, 1995). Some controversy exists over the affinity of the Aberdeen Formation; previous studies suggested that it was part of the Argyll Group (Munro, 1986), whereas more recently it has been interpreted to be part of the Southern Highland Group (Gould, 1997; Stephenson and Gould, 1995). Based on gradational contacts between the granites and their country rocks it has been suggested that the magmas were generated more or less in-situ (Kneller and Aftalion, 1987; Richardson and Powell, 1976), by melting of the host metasedimentary rocks. However, as the granites vary greatly in size (Kemnay: ~36 km<sup>2</sup>; Cove: ~1.7 km<sup>2</sup>; Nigg Bay: even smaller than the Cove Granite), it is quite likely that the larger granite bodies also contain material of source(s) located at deeper levels in the crust.

U-Pb dating of magmatic zircons from the Kemnay, Cove and Nigg Bay granites shows that all three crystallised at approximately the same time at  $457 \pm 3$  Ma,  $458 \pm 5$  Ma and  $465 \pm 5$  Ma, respectively, shortly after the peak of regional metamorphism



at 470 Ma (e.g. Strachan et al., 2002). Inherited cores, which occur in 60-95 % of all analysed zircon crystals, yield similar concordant  $^{207}\text{Pb}/^{206}\text{Pb}$  of c. 1.8 to 1.05 Ga in the Kemnay Granite, c. 1.5 to 1.0 Ga in the Cove Granite and c. 1.6 to 0.9 Ga in the Nigg Bay Granite. When the data are considered collectively, dominant peaks exist at c. 1.45 Ga and 1.05-1.0 Ga. Discordant ages form an additional peak at c. 2.7-2.5 Ga. These age ranges are essentially the same as those reported for detrital zircons from the Dalradian Supergroup (Cawood et al., 2003).

$\epsilon\text{Hf}$  values of magmatic zircons are broadly similar amongst the granites (Kemnay: -9.9 to -17.3; Cove: -12.6 to -20.3; Nigg Bay: -12.2 to -18.5) and overlap with Hf isotope data calculated from published Nd isotope data of the Dalradian Appin and Argyll groups. The U-Pb data of inherited cores and the Hf isotope data of magmatic zircons therefore suggest that the three granites share the same source material, most likely their current Dalradian Supergroup country rocks.

However, zircon oxygen isotope data reveal large differences between the granites (Fig. 12). Magmatic zircons from the Kemnay Granite span a large range of values between 7.0 ‰ and 12.0 ‰ (mean = 9.2 ‰). Inherited cores show an even larger spread between 6.7 ‰ and 13.3 ‰. Resolvable intra-grain variation was detected in one crystal, which comprises a magmatic core of 7.7 ‰ and a rim of 9.1 ‰. In contrast, magmatic and inherited zircon crystals from the Cove Granite form much more homogeneous oxygen isotope populations, and display values between 8.8 ‰ and 11.6 ‰ (mean = 10.0 ‰), and 6.9 ‰ and 9.0 ‰ (mean = 7.6 ‰), respectively. Inherited and magmatic zircons of the Nigg Bay Granite are even more homogeneous, and in addition considerably less evolved with  $\delta^{18}\text{O}$  values of magmatic zircons between 6.1 ‰ and 8.4 ‰ (mean = 7.3 ‰) and of inherited cores between 4.1 ‰ and 7.7 ‰ (one outlier at 9.7 ‰, mean = 5.8 ‰). Intra-grain variations were not detected in zircons of either the Cove or Nigg Bay granites. Based on these data the Kemnay and Cove granites display compositions typical of S-type granites, whereas the Nigg Bay Granite shows  $\delta^{18}\text{O}$  values more commonly observed in I-type granites (Papers 1 and 2), which suggests that the granites did not melt the same source materials.

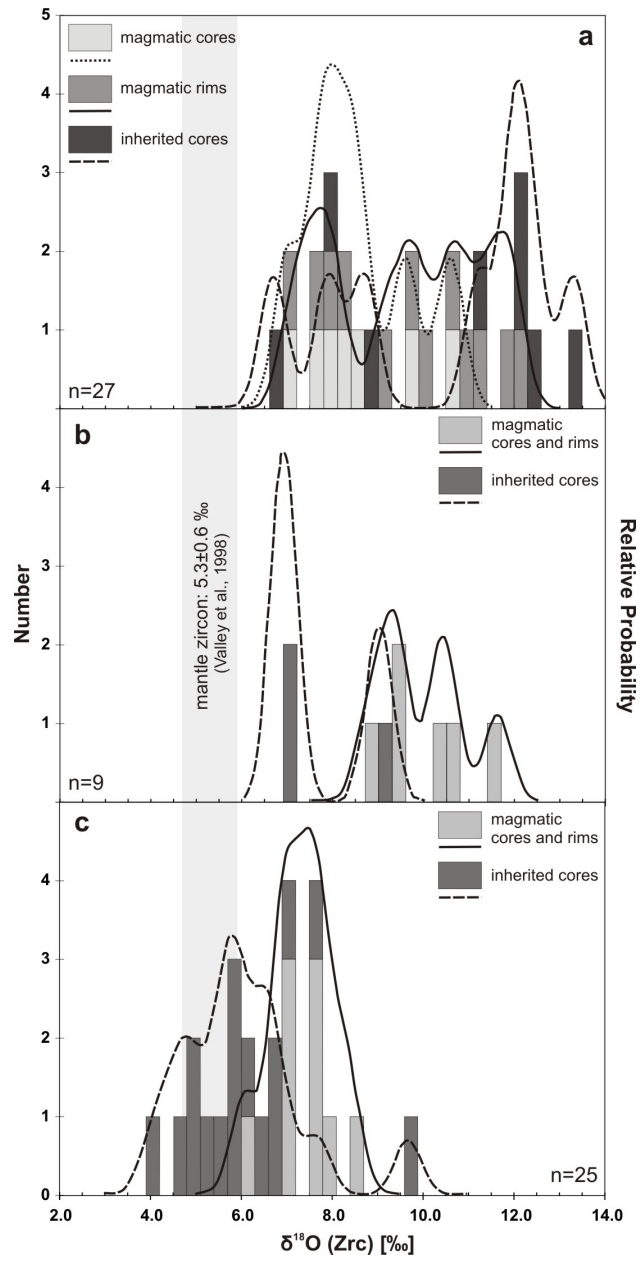


Fig. 12: Cumulative probability plots of zircon oxygen isotope data (probability curves and histograms were calculated at  $1\sigma$ ) from the Kemnay, Cove and Nigg Bay S-type granites.

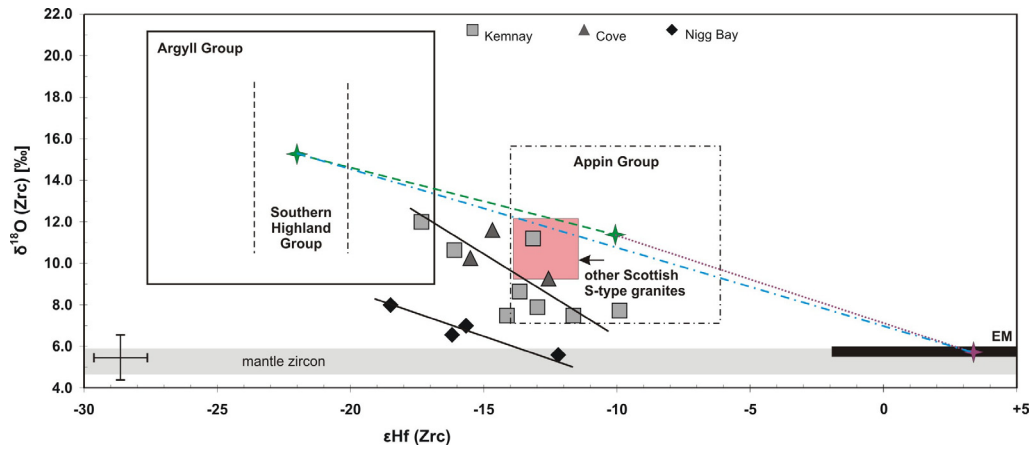


Fig. 13:  $\epsilon\text{Hf}$  values (at emplacement age) vs.  $\delta^{18}\text{O}$  of magmatic zircons of the Kemnay, Cove and Nigg Bay granites (precision on zircon  $\delta^{18}\text{O}$  and  $\epsilon\text{Hf}$  = 0.6 ‰ and 1.0 units ( $2\sigma$ ), respectively). Also shown are fields for whole-rock  $\delta^{18}\text{O}$  and estimated  $\epsilon\text{Hf}$  data of the Appin, Argyll and Southern Highland groups, and other Scottish S-type granites (data from Anderson et al., 2004; Frost and O'Nions, 1985; Halliday, 1984; Hamilton et al., 1980; Harmon, 1983; Kay, 1980; O'Nions et al., 1983) and mixing lines (green, purple and blue) between the potential end-members.

Plotting the data of the Kemnay, Cove and Nigg Bay granites in an  $\epsilon\text{Hf}$  vs.  $\delta^{18}\text{O}$  diagram (Fig. 13) shows that all three lie on two negatively-sloping linear mixing trends, which partly overlap fields for the Argyll and (stratigraphically older) Appin groups. These trends may be explained in one of three ways: (1) All three granites sourced rocks of the Argyll and Appin groups, possibly at lower lithostratigraphical and structural levels than their Aberdeen Formation host rocks. In the Cove and Nigg Bay granites melts mixed thoroughly, which led to homogenous oxygen isotope compositions, whereas incomplete mixing resulted in the oxygen isotope heterogeneities observed in the Kemnay Granite. The low  $\delta^{18}\text{O}$  values observed in the Nigg Bay Granite were produced by melting of a local low- $\delta^{18}\text{O}$ , possibly hydrothermally altered, unit within the Appin or Argyll groups. (2) Only the Kemnay and Cove granites were generated by melting of Appin Group and Argyll  $\pm$  Southern Highland Group rocks. The Nigg Bay Granite formed by mixing between Argyll  $\pm$  Southern Highland Group rocks and an infracrustal source with primitive, mantle-like oxygen and crustal Hf isotope characteristics. (3) All three granites comprise a mixture of melts derived from a mafic lower crustal source and a supracrustal component, possibly the Aberdeen Formation. Based on the high proportion of low- $\delta^{18}\text{O}$  zircons the Nigg Bay Granite comprises a larger infracrustal component

whereas the Kemnay and Cove granites contain higher proportions of a supracrustal source. Involvement of pristine contemporaneous Lower Palaeozoic mantle can be precluded on the base of Hf isotope data.

To fully resolve the origin and evolution of the Kemnay, Cove and Nigg Bay granites a more extensive study is required. Nevertheless, this pilot study of S-type granites shows that either supracrustal materials do not always have evolved oxygen isotope compositions, or alternatively that S-type granites, even if compositionally very similar, have complex petrogenetic histories and possibly comprise multiple sources.

# **II.**

## **PAPER 1**

**A cryptic record of magma mixing in  
diorites revealed by high-precision SIMS  
oxygen isotope analysis of zircons**

# A cryptic record of magma mixing in diorites revealed by high-precision SIMS oxygen isotope analysis of zircons

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## Abstract

High-precision in-situ ion microprobe (SIMS) oxygen isotope analysis of zircons from two diorite intrusions associated with the late Caledonian Lochnagar pluton in Scotland has revealed large differences in the degree of heterogeneity in zircon  $\delta^{18}\text{O}$  between the diorites. Zircon crystals from the Cul nan Gad diorite (CnG) show a unimodal distribution of oxygen isotope values ( $\delta^{18}\text{O} = 6.0 \pm 0.6 \text{‰}$  ( $2\sigma$ )) and no or only minor grain-scale variation. Those from the Allt Darrarie diorite (AD1) show a large range in  $\delta^{18}\text{O}$  and an apparent bimodal distribution with modes of  $6.6 \pm 0.4 \text{‰}$  and  $7.3 \pm 0.4 \text{‰}$ . Variations of up to  $1.2 \text{‰}$  occur between and within grains; both an increase and decrease in  $\delta^{18}\text{O}$  with zircon growth has been observed. The  $\delta^{18}\text{O}$  composition of growing zircon can only change if open-system processes affect the magma composition, i.e. if material of contrasting  $\delta^{18}\text{O}$  composition is added to the magma. The variability in AD1 is interpreted to represent a cryptic record of magma mixing. A ‘deep crustal hot zone’ is a likely site for generation of the dioritic magmas which developed by mixing of residual melts and crustal partial melts or by

melting of mafic lower crustal rocks. The overall small number of zircons with mantle-like  $\delta^{18}\text{O}$  values ( $5.3 \pm 0.6 \text{ ‰}$  ( $2\sigma$ )) in the Lochnagar diorites is largely the product of crustal differentiation rather than crustal growth.

The  $\delta^{18}\text{O}$  of quartz from the CnG and AD1 diorites shows only minor variation (CnG:  $10.9 \pm 0.5 \text{ ‰}$  ( $2\sigma$ ), AD1:  $11.7 \pm 0.6 \text{ ‰}$  ( $2\sigma$ )) within single populations, with no evidence of mixing. Quartz-zircon isotopic disequilibrium is consistent with later crystallisation of quartz from late magmatic fluids, and in case of the AD1 diorite after the inferred magma mixing from a homogenised, higher  $\delta^{18}\text{O}$  melt.

High-precision SIMS oxygen isotope analysis of zircon provides a new approach to identifying and resolving previously undetected early-stage magma mixing and constraining the compositions and origins of the component magmas. A combination of zircon, quartz and whole-rock data has proven to be a powerful tool in reconstructing the petrogenetic evolution of diorite from early crystallisation to late alteration.

## 1. Introduction

Oxygen isotopes have been widely used in petrogenetic evolution studies of granitic rocks to constrain the relative contributions of mantle and crust and the roles of fractional crystallisation, assimilation and magma mixing. The oxygen isotope compositions of granites and their constituent minerals are sensitive to modification by assimilation of  $^{18}\text{O}$ -enriched crustal rocks, magma mixing and/or hydrothermal alteration by  $^{18}\text{O}$ -depleted fluids (e.g. King et al., 1997, 2000; Monani and Valley, 2001; Valley and Graham, 1996).

Zircon is a common accessory mineral in intermediate and silicic plutonic rocks. Due to extremely slow rates of oxygen diffusion and high closure temperatures (Dodson, 1973; Peck et al., 2003; Valley, 2003; Watson and Cherniak, 1997) it is insensitive to hydrothermal alteration and fractional crystallisation during cooling, and therefore retains its oxygen isotope composition from the time of crystallisation (e.g. Kemp et al., 2005a, 2005b, 2006, 2007; King et al., 1998, 2002, 2004; King and Valley, 2001; Lackey et al., 2005, 2006). New developments in micro-analytical techniques now permit the rapid in-situ analysis of oxygen isotopes in zircon at high precision (here 0.4-0.6 ‰ ( $2\sigma$ )) by ion microprobe. With a beam diameter of only c. 20  $\mu\text{m}$ , multiple analyses may be made in a single zircon crystal, which enables detection of differences in  $\delta^{18}\text{O}$  between growth zones and between cores and rims in individual crystals, and allows detailed comparison between crystals. The high analytical precision and high spatial resolution of modern ion microprobes offers the potential to identify previously undetectable variations in oxygen isotope composition, providing more detailed insights into granite magma genesis and evolution.

Quartz, which commonly crystallises in the later stages of magmatic evolution, is also more resistant to isotopic modification than its host rock, and hence may also preserve isotopic signatures derived directly from the melt (e.g. Bindeman and Valley, 2001; Criss and Taylor, 1986; Monani and Valley, 2001; Valley et al., 1994). Conventional laser fluorination oxygen isotope data have commonly been used to assess the state of equilibrium between zircon, quartz and whole-rock samples in silicic magmatic rocks as a useful guide to the petrological and geochemical



evolution of magmas and rocks (King et al., 1997, 1998, 2004; King and Valley, 2001; Lackey et al., 2005, 2006; Monani and Valley, 2001).

This paper presents high-precision in-situ ion microprobe oxygen isotope data for zircon and quartz, supported by whole-rock  $\delta^{18}\text{O}$  analyses, from two diorite intrusions forming part of the late Caledonian (424-413 Ma) (Paper 2) Lochnagar pluton in Scotland. It introduces a new approach to deciphering the detailed grain-scale petrogenetic information stored in zircon and quartz, and tests the results against recent models for the generation and evolution of intermediate and silicic calc-alkaline igneous rocks (e.g. Annen et al., 2006).

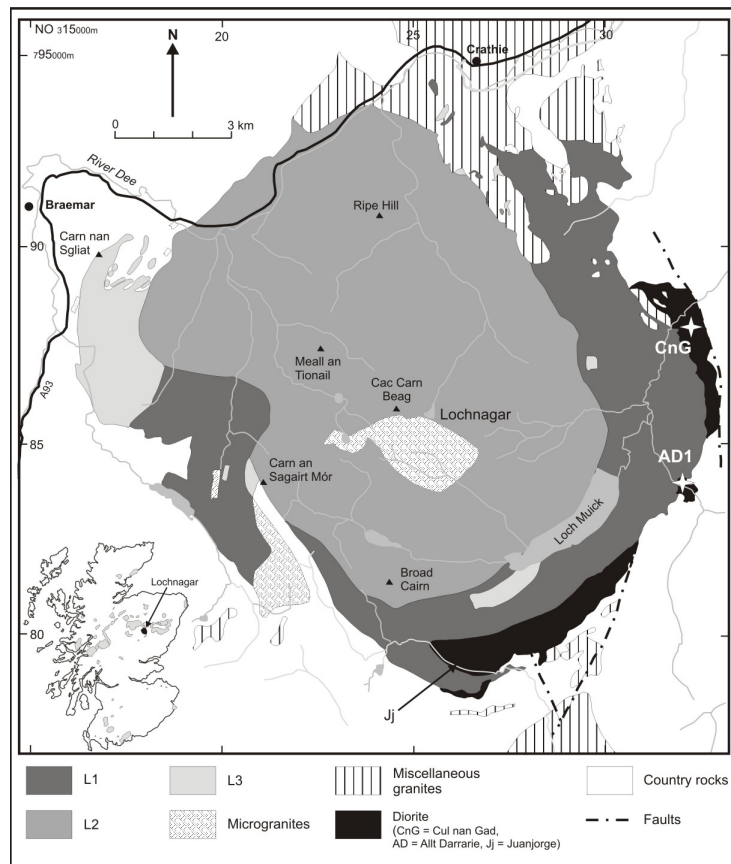


Fig. 1: Geological sketch map of the Lochnagar pluton (after Smith et al., 2001). Lochnagar comprises three main granite (L1, L2, L3) intrusions, several marginal diorite intrusions and late intrusions of microgranite. This paper focuses on the Cul nan Gad (CnG) and Allt Darrarie (AD1) diorites (stars indicate sample locations).

## 2. Geological background and sample details

The Lochnagar pluton, which crops out over an area of c. 150 km<sup>2</sup>, is located in the Grampian Highlands of Scotland and belongs to the classic suite of late Caledonian 'I-type' intrusions that were emplaced at 430-400 Ma, after the c. 470 Ma Grampian Event and broadly contemporaneously with the oblique collision of Baltica and Laurentia (the Scandian Event) (Coward, 1990; Dallmeyer et al., 2001; Dewey and Mange, 1999; Kinny et al., 2003). However, the connection between this collision and the voluminous I-type magmatism is unclear. Based on field relationships and whole-rock geochemical and isotopic data, the Lochnagar pluton has been described as composite, comprising three main granite facies (L1, L2, L3) distinguished by textural and modal variations, a late intrusion of microgranite, and several marginal intrusions of diorite (Fig. 1) (Halliday, 1984; Halliday et al., 1979; Oldershaw, 1974; Smith et al., 2001). Two small diorite intrusions, Cul nan Gad (CnG) and Allt Darrarie (AD1) (with areal dimensions of 4.5 x 1.8 km (CnG) and 0.6 x 0.4 km (AD1); Smith et al. 2001), are the subject of this study. Based on field relationships these were interpreted to be consanguineous with, but cut by, the granite (Smith et al. 2001).

The diorites are dark grey, fine- to medium-grained (< 1-3 mm), and have a calc-alkaline metaluminous composition. They comprise plagioclase (45-50 %), biotite (c. 40 %), hornblende (< 5-10 %) and interstitial quartz (c. 5 %), with accessory ilmenite and magnetite, titanite (absent in CnG), zircon and apatite. All minerals are distributed evenly, which suggests that they do not contain cumulate or restite material and that the diorites represent melt compositions. Plagioclase crystals are sometimes zoned, commonly twinned and weakly altered to sericite in the centre. Biotites are often partially or entirely altered to chlorite, which is particularly prominent in the CnG diorite.

### 3. Methodology

#### 3.1. Zircon sample preparation

Zircon separation was carried out at the University of St. Andrews Mineral Separation Facility. Rock samples of approximately 5 kg were crushed and sieved to obtain the < 500 µm fraction from which zircon crystals were separated using a Wilfley Table, heavy liquids and a Frantz magnetic separator. Approximately 100 zircon crystals were hand-picked from the remaining heavy, non-magnetic fraction, providing a range of grain size, morphology, transparency, alteration and occurrence of inclusions or cracks. The crystals were mounted into epoxy (Araldite) and the zircon mounts polished to about half thickness to expose the crystal interiors. The polished surfaces were imaged in secondary electron (SE), back-scattered electron (BSE) and cathodoluminescence (CL) mode using a Philips XL30CP Scanning Electron Microscope (SEM) at the University of Edinburgh to identify internal zoning features, inherited material, inclusions and cracks. Suitable crystals for in-situ oxygen isotope analysis were selected using this information.

#### 3.2. Zircon SIMS oxygen isotope analysis

Zircon oxygen isotope data were obtained using a Cameca ims-1270 ion microprobe at the University of Edinburgh following the methods of Cavosie et al. (2005) and Kemp et al. (2006). A 6nA primary  $^{133}\text{Cs}^+$  ion beam with a diameter of c. 20 µm was used, charge was neutralised using a normal-incidence electron flood gun, secondary ions were extracted at 10 kV, and  $^{18}\text{O}^-$  and  $^{16}\text{O}^-$  ions were monitored simultaneously on dual Faraday cups. Secondary ion beam centring, pre-sputtering for 50 seconds and subsequent data collection over 10 cycles (total counting time: 40 seconds = 4 seconds per cycle) resulted in a total acquisition time of c. 200 seconds. The secondary yield of  $^{18}\text{O}$  under these conditions was typically between  $4.5 \times 10^6$  and  $5.5 \times 10^6$  counts per second. To correct for instrumental mass fractionation (IMF) and instrumental drift, all data were normalised to zircon standard 91500 ( $\delta^{18}\text{O} = 9.86 \text{ ‰}$ ) (Wiedenbeck et al., 2004), which was analysed in blocks of 5 to 10

after every 10 to 15 unknown zircon analyses. During stable instrument conditions the unknown zircon analyses were normalised to the daily average  $^{18}\text{O}/^{16}\text{O}$  value obtained for 91500. In cases where instrumental drift was recognised, the analytical conditions changed or sample exchange was carried out, the data were divided into sessions in which unknowns were normalised to the linearly interpolated  $^{18}\text{O}/^{16}\text{O}$  value derived from analyses of the bracketing 91500 standard.

Prior to oxygen isotope analysis,  $\text{HfO}_2$  concentrations in the zircons were measured by electron microprobe as variations in  $\text{HfO}_2$  have been shown to cause variations in IMF (Peck et al., 2001). This has been shown to be particularly important when conducting analysis using e.g. a Cameca ims-4f at high-energy offset. However, in this study oxygen isotope analysis were carried out using a Cameca ims-1270 ion microprobe, and in both diorite samples  $\text{HfO}_2$  variations in zircons were  $\leq 0.5$  wt %; therefore corrections for IMF were unnecessary. The internal precision of individual point analyses based on counting statistics varied between 0.1-0.2 ‰. External precision based on the reproducibility of standard 91500 ranged from 0.4 ‰ (n=57) to 0.6 ‰ (n=38) (2SD) and 0.040 to 0.087 (1 s.e.m.).

Analyses were conducted in clear, crack- and inclusion-free areas of representative zircon crystals. Where possible, multiple analyses (core to rim) were carried out on single zircon crystals to document zircon growth histories, and occasionally also in adjacent spots within crystals to assess reproducibility. The ion probe pits were subsequently imaged in BSE and SE mode using an SEM to determine the exact position of the analyses and to ensure that no cracks in the bottom of the pit might have influenced the results. Data obtained from suspect locations were rejected. In addition, data were excluded when the correction on the position of the secondary ion beam was anomalously large.

### *3.3. Quartz SIMS oxygen isotope analysis*

Oxygen isotope analysis of quartz was carried out on polished thin sections using the Cameca ims-1270 ion microprobe, employing the same instrument set-up as for zircon oxygen isotope analysis. Quartz data were normalised to quartz standard

NBS28 ( $\delta^{18}\text{O} = 9.58 \text{ ‰}$ ) (National Institute of Standards & Technology, 1992), which was analysed after every 15-20 unknowns. Internal precision calculated from NBS28 varied between 0.1 ‰ and 0.2 ‰. The external precision was 1.1 ‰ (2SD,  $n=59$ ) and 0.072 (1 s.e.m.). In comparison, uncertainties on the unknowns were considerably lower (0.5 ‰ ( $n=22$ ) and 0.6 ‰ ( $n=27$ ) (2SD), 0.057 (1 s.e.m.) for CnG and AD1 respectively). Thus, the uncertainties on the unknown quartz crystals most closely reflect the analytical precision.

Where possible, multiple ion microprobe analyses were obtained between the centre and edge of each crystal in order to identify potential oxygen isotope zoning arising either from changes in the magma chemistry or from oxygen volume diffusion.

### *3.4. Whole-rock analyses*

Oxygen isotope analyses of whole-rock samples were carried out at the Scottish Universities Environmental Research Centre (SUERC) at East Kilbride following the Macaulay et al. (2000) modification of the laser fluorination methodology of Sharp (1990). Approximately 1 mg of powdered sample was reacted with  $\text{ClF}_3$  whilst being heated with a  $\text{CO}_2$  laser. The resultant oxygen was purified, converted to  $\text{CO}_2$  on platinised graphite, and the yield measured with a capacitance manometer. The oxygen isotope composition of the  $\text{CO}_2$  was measured by a Micromass PRISM 3 dual inlet, triple collector mass spectrometer with a working standard gas calibrated against international reference materials. The accuracy and precision are  $\pm 0.4 \text{ ‰}$  ( $2\sigma$ ), and NBS28 gives a value of 9.56 ‰.

Major element concentrations were determined at the University of Edinburgh using a PANalytical PW2404 wavelength-dispersive sequential X-ray spectrometer.

## 4. Results

### 4.1. Zircon description

Zircon crystals show a similar range of sizes, morphologies and internal zoning textures in both diorites. This is a common phenomenon and is generally interpreted to be the result of varying local kinetic factors such as diffusion rates and adsorption (Dowty, 1980; Vavra, 1990, 1993). The only obvious difference between CnG and AD1 zircons lies in their CL character. AD1 zircons are overall more strongly luminescent and usually show only smaller luminescence contrast between growth zones.

In both diorite samples zircons vary in size between c. 200  $\mu\text{m}$  and  $\geq 700 \mu\text{m}$  along the c-axis, and have equant, stubby and elongated morphologies (aspect ratios AD1: 1:1.1 to  $1:\geq 5.6$ , CnG: 1:1.2 to  $1:1:\geq 7.3$ ) with stubby and elongated crystals being dominant. With respect to internal zoning, all zircons consist of a core, which usually comprises most of the crystal, and up to three mantles and a rim varying in width from c. 5  $\mu\text{m}$  to 100  $\mu\text{m}$ . Cores, mantles and rims, are separated by resorption surfaces, which are generally interpreted to reflect periods of Zr undersaturation in the magma for which the dominant controls are either large-scale mixing events or local kinetic phenomena (Corfu et al., 2003). U-Pb dating by ion microprobe has shown that none of these cores contains inherited (significantly older) components. Hence, they represent magmatic cores that precipitated from the diorite magma, but reflect a different (early) evolution stage than the surrounding rims. Magmatic cores are either completely unzoned (c1) (Fig. 2a), comprise a relatively large inner unzoned domain (c1) and a surrounding outer oscillatory zoned domain (c2) (Fig. 2b-d) or appear to be entirely zoned (c2) (Fig. 2e). In the latter case a c1 domain is usually either difficult or impossible to identify. In terms of CL intensity, c1 domains are always moderately to weakly luminescent, whereas zones within the c2 domain vary between strongly and weakly luminescent. Mantles and rims consist of either a single or multiple zones.

Based on these characteristics it is likely that both diorites contain only a single zircon population in which c1, c2 and the surrounding mantles and rims vary in size due to local differences in growth rate or Zr saturation level in the magma.

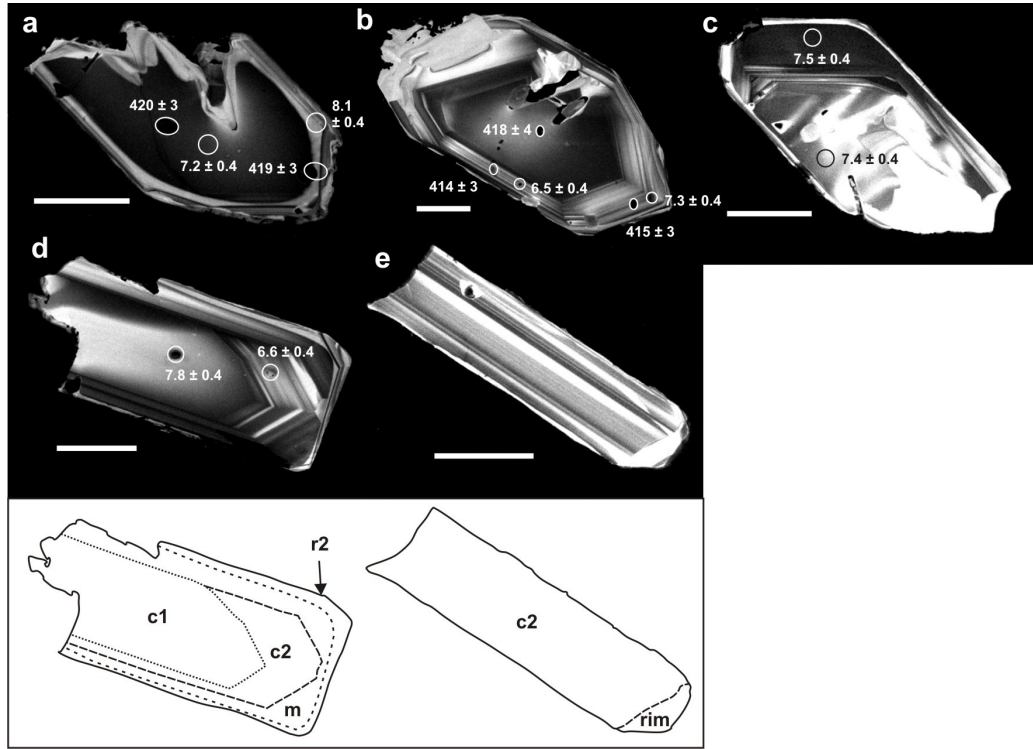


Fig. 2: CL images of zircon crystals representative of zircons from the CnG and AD1 diorites with oxygen isotope and U-Pb data (circles indicate position of oxygen isotope analyses, ovals of U-Pb analyses; error on  $\delta^{18}\text{O}$  is  $\pm 0.4\text{‰}$  ( $2\sigma$ ); scale bar = 50  $\mu\text{m}$ ).

- a) Zircon grain (AD1 grain 11) consisting of large resorbed, weakly luminescent core (c1) and moderately luminescent rim. Note the large increase in  $\delta^{18}\text{O}$  between core and rim.
- b) Crystal (AD1 grain 9) comprises weakly luminescent unzoned inner core (c1), oscillatory zoned outer core (c2) and a rim. Both  $\delta^{18}\text{O}$  values are from within c2, but vary by 0.8‰.
- c) Zircon (AD1 grain 5) shows similar zoning pattern as b), but has two resorption surfaces. Core and rim analyses are identical within error.
- d) Zoning is similar to b) and c) with c1, c2, mantles (m) and a rim (AD1 grain 10). Here c1 is 1.2‰ higher than c2, thus zoning is opposite to a).
- e) Zircon grain lacks obvious c1 core domain (AD1 grain 17).

#### 4.2. Zircon oxygen isotope data

All oxygen isotope values reported here are in per mil (‰) and relative to VSMOW (Vienna Standard Mean Ocean Water). Oxygen isotope data are presented in Figures 3a and 4a as histograms with overlaid cumulative probability curves, which were calculated by summing the probability distributions of a suite of data

with normally distributed errors (Isoplot ver.3.00, Ludwig, 2003). The bin widths of the histograms were chosen according to the precision ( $1\sigma$ ) obtained from analyses of standard 91500 in the same analytical session, as this best represents the instrument performance during each session. Heterogeneities larger than those detected in 91500, which is assumed to be homogeneous in  $\delta^{18}\text{O}$ , are considered to reflect real variations in oxygen isotope composition. The data are also shown in grain-scale variation plots (Fig. 3c & 4c) to establish whether heterogeneities mainly occur between or within grains; these diagrams also illustrate whether the data lie within the error of the mean.

The  $\delta^{18}\text{O}$  values of zircons from CnG lie between 5.5 ‰ and 6.4 ‰, with a mean value of 6.0 ‰ ( $n=36$ ) and a standard deviation of 0.6 ‰ (2SD) (Table 1, Appendix 1). Zircon standard 91500 analysed in the same analytical session displays the same standard deviation ( $n=38$ ) and degree of heterogeneity (2SD = 0.6 ‰). From this we interpret that the analytical precision of this session approximates 0.6 ‰ ( $2\sigma$ ). The cumulative probability-histogram for CnG (Fig. 3a) shows a unimodal distribution with a mode of 5.9 ‰; a similar distribution is observed for 91500. Neither intra-grain and inter-grain variations in  $\delta^{18}\text{O}$  nor systematic differences between cores, mantles and rims were detected (Fig. 3b). The grain-scale variation plot (Fig. 3c) reveals that all analyses lie within  $2\sigma$  error of the mean and that only minor variation exists between and within crystals. However, these variations are not resolvable within the limits of analytical uncertainty.

Zircons from AD1 are relatively enriched in  $^{18}\text{O}$  and display a much larger range in  $\delta^{18}\text{O}$  than those from CnG, ranging from 6.1 ‰ to 8.1 ‰ with a mean of 7.1 ‰ ( $n=41$ ). A standard deviation of 0.9 ‰ (2SD) is more than twice as large as for the 91500 standard analysed in the same analytical session (0.4 ‰, 2SD,  $n=57$ ) and must therefore be considered to represent real isotopic heterogeneity. The cumulative probability-histogram (Fig. 4a) shows an apparent bimodal distribution with partly overlapping modes of 6.6 ‰ and 7.3 ‰. Based on this observation the data were separated into two apparent oxygen isotope populations with mean  $\delta^{18}\text{O}$  values of  $6.6 \pm 0.4$  ‰ (population 1,  $2\sigma$ ) and  $7.4 \pm 0.4$  ‰ (population 2,  $2\sigma$ ). Plotting the probability-histogram of the same data separated into c1, c2 core domains, and mantles and rims (Fig. 4b) shows that each textural component (cores, rims etc.) also



displays a bimodal distribution. Thus, bimodality in AD1 cannot be attributed to systematic intra-grain differences or zonations in  $\delta^{18}\text{O}$ . The grain-scale variation plot reveals that, as indicated by the cumulative probability-histogram, several values lie above and below the field defining the  $2\sigma$  error of the mean for the whole AD1 data set (Fig. 4c). It also demonstrates that the large range in values results from variations both between grains (e.g. grain 16: 6.1-6.5 ‰, grain 11: 7.2-8.1 ‰) and within grains (core-mantle/rim, c1-c2 core domains and even within core domains). The largest *intra-grain* variation of 1.2 ‰ in grain 10 occurs between c1 (7.8 ‰) and c2 (6.6 ‰) core domains, and represents only about half of the full range of variation of  $\delta^{18}\text{O}$  in AD1 zircons. The largest variation *between a magmatic core and rim* can be observed in grain 11 (0.9 ‰) (core: 7.2 ‰, rim: 8.1 ‰) (Fig. 2a) and the largest range *within a single domain* in grain 9 (c2a: 6.5‰, c2b: 7.3‰) (Fig. 2b). This demonstrates that changes in  $\delta^{18}\text{O}$  do not always conform to occurrence of resorption surfaces, but also exist within a single zone. Evidence was also found of cores and rims in some zircon crystals showing no - only minor - intra-grain variations, such as grain 5 (core: 7.4 ‰, rim: 7.5‰), despite being separated by resorption surfaces (Fig. 2c). Commonly AD1 zircon crystals show an increase in  $\delta^{18}\text{O}$  with zircon growth in grains where multiple analyses (core to rim) were carried out, but grain 10 very clearly displays the opposite trend (Fig. 2d).

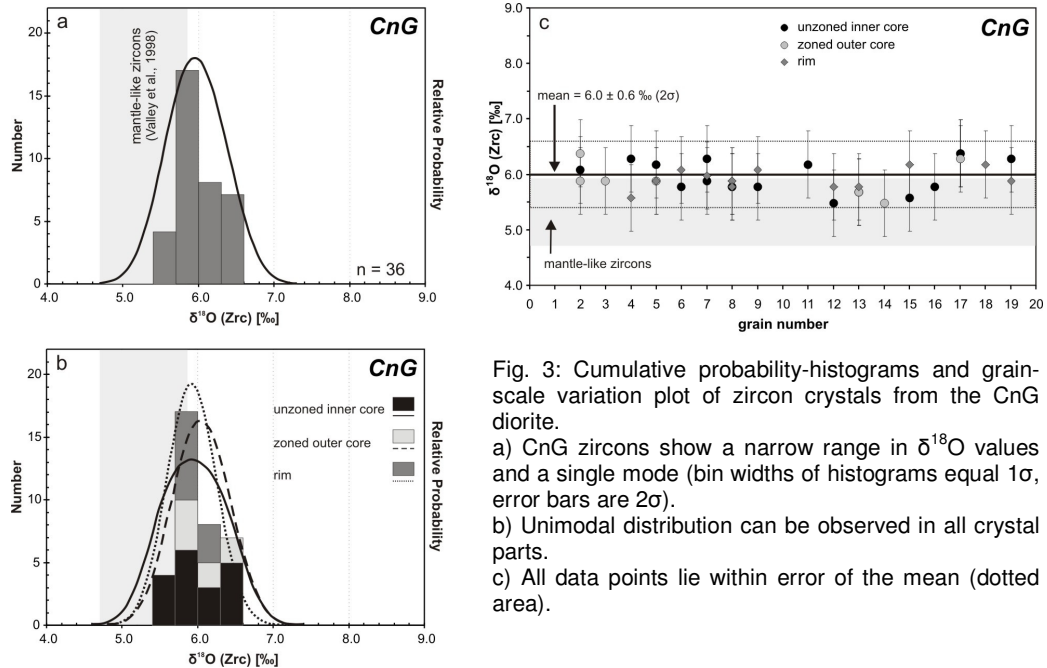


Fig. 3: Cumulative probability-histograms and grain-scale variation plot of zircon crystals from the CnG diorite.  
a) CnG zircons show a narrow range in  $\delta^{18}\text{O}$  values and a single mode (bin widths of histograms equal 1 $\sigma$ , error bars are 2 $\sigma$ ).  
b) Unimodal distribution can be observed in all crystal parts.  
c) All data points lie within error of the mean (dotted area).

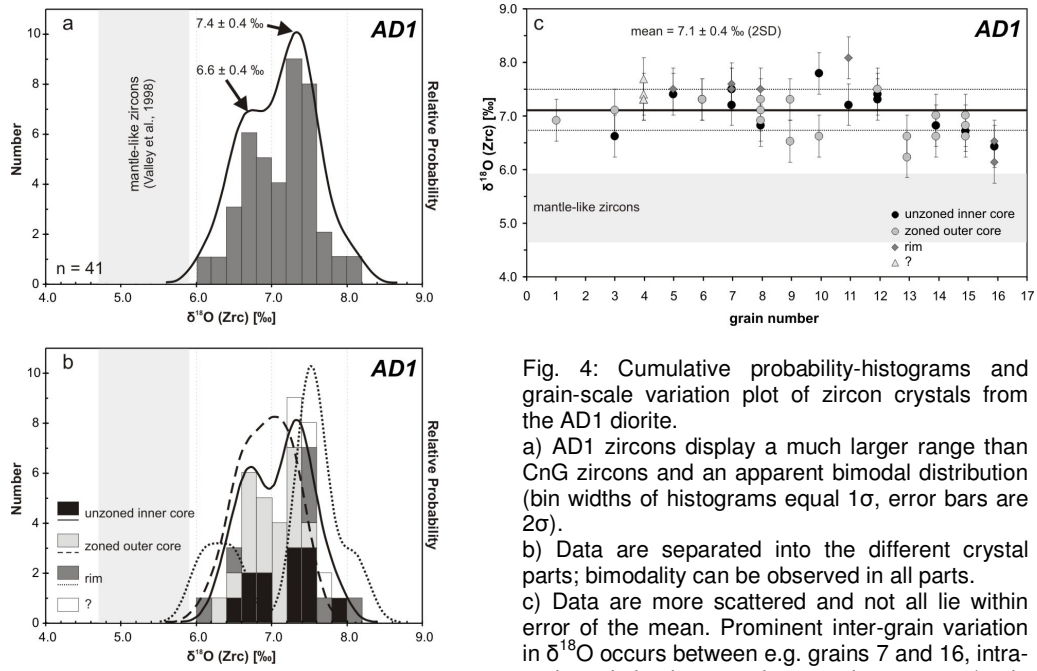


Fig. 4: Cumulative probability-histograms and grain-scale variation plot of zircon crystals from the AD1 diorite.

a) AD1 zircons display a much larger range than CnG zircons and an apparent bimodal distribution (bin widths of histograms equal  $1\sigma$ , error bars are  $2\sigma$ ).

b) Data are separated into the different crystal parts; bimodality can be observed in all parts.

c) Data are more scattered and not all lie within error of the mean. Prominent inter-grain variation in  $\delta^{18}\text{O}$  occurs between e.g. grains 7 and 16, intra-grain variation between inner and outer core (grain 9), core and rim (grain 11).  $\delta^{18}\text{O}$  commonly increases with zircon growth except in grain 10.

#### 4.3. Quartz oxygen isotope data

In both intrusions, quartz crystals from tens of microns to approximately 1 mm are weakly to moderately luminescent. Almost all crystals have annealed and open cracks, with typically more weakly luminescent areas along them (Fig. 5); these are a common feature in quartz crystals (e.g. Valley and Graham, 1996). CL evidence of growth zoning was not generally observed, but numerous crystals have weakly luminescent rims.

CnG quartz oxygen isotope data range from 10.4 ‰ to 11.4 ‰ with a mean of  $10.9 \pm 0.5$  ‰ (2SD,  $n=22$ ) (Table 1, Appendix 2). One analysis in a weakly luminescent (possibly hydrothermally altered) area yields a value of 12.0 ‰. AD1 quartz oxygen isotope values range from 11.3 ‰ to 12.3 ‰ with a mean of  $11.7 \pm 0.6$  ‰ (2SD,  $n=27$ ). The values from both samples display unimodal distributions (Fig. 7), and all data other than the possibly altered sample lie within error of the mean. A systematic change in composition between grain centres and rims or between grain sizes was not observed.

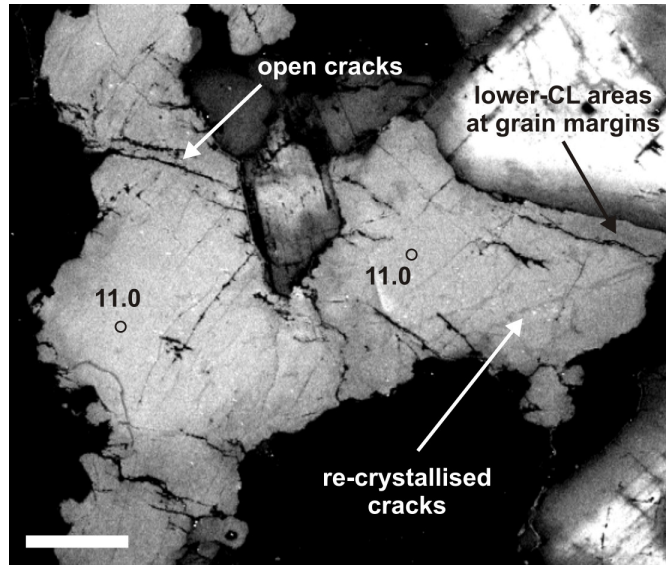


Fig. 5: CL image of representative quartz crystal (CnG, grain 9) with oxygen isotope data. Quartz contains open and re-crystallised cracks as well as lower-CL areas along its grain margins. Error:  $\pm 0.5\text{‰}$  ( $2\sigma$ ), scale bar = 200  $\mu\text{m}$ .

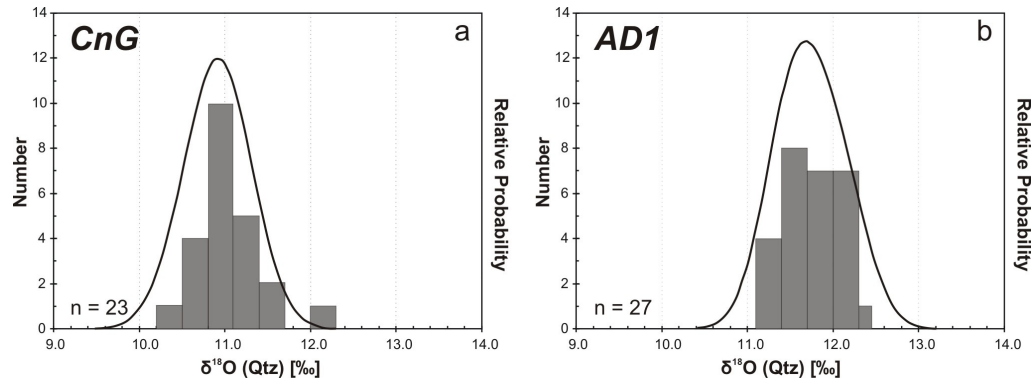


Fig. 6: Cumulative probability-histograms of quartz  $\delta^{18}\text{O}$  data. Both diorites comprise single quartz populations. Outlier in CnG represents analysis on altered area along a microcrack.

Table 1

$\delta^{18}\text{O}$  values and fractionation factors for Lochnagar diorites

Sample	SiO <sub>2</sub> [wt%]	$\delta^{18}\text{O}$ (Zrc) [‰]	$2\sigma$	n	$\delta^{18}\text{O}$ (WR) [‰]	$2\sigma$	n	$\delta^{18}\text{O}$ (Qtz) [‰]	$2\sigma$	n	$\Delta(\text{Zrc-WR})$ [‰]	$\Delta(\text{Qtz-Zrc})$ [‰]	$2\sigma$
CnG	54.6	6.0	0.6	36	7.2	0.4	2	10.9	0.5	17	-1.8 to -0.6	+4.9	1.1
AD1	53.0	7.1	0.4	41	7.0	0.4	2	11.7	0.6	22	-0.3 to +0.5	+5.6 to +3.6	1.0

## 5. Discussion

The results of this study show that zircon crystals from the Lochnagar diorites display significant differences in their degree of isotopic heterogeneity. All zircons from the CnG diorite sample are homogeneous (within  $2\sigma$  error of the mean) in their oxygen isotope composition, with a population mean of  $6.0 \pm 0.6 \text{ ‰}$  ( $2\sigma$ ). Those from the AD1 diorite are heterogeneous and yield two apparent populations of  $6.6 \pm 0.4 \text{ ‰}$  and  $7.4 \pm 0.4 \text{ ‰}$ .

Comparison of the  $\delta^{18}\text{O}$  of zircons with those of co-existing quartz and their host whole-rocks may be used to assess whether any of the oxygen isotope populations revealed in zircon are in isotopic equilibrium with either quartz or host rocks. In addition, it enables us to resolve the contrasting magmatic evolution and processes of the two diorites in more detail.

### 5.1. Whole-rock – zircon equilibrium fractionation

Equilibrium oxygen isotope fractionation factors between whole-rock and zircon  $\Delta(\text{WR-Zrc})$  vary systematically with temperature and  $\text{SiO}_2$  concentration (Valley et al., 1994, 2005). Higher silica concentrations in more evolved rocks reflect higher abundances of quartz and feldspar, which are enriched in  $^{18}\text{O}$  relative to zircon and responsible for higher whole-rock  $\delta^{18}\text{O}$  values. Hence,  $\Delta(\text{WR-Zrc})$  at any temperature increases with increasing whole-rock  $\text{SiO}_2$  content. Differentiation in magmas therefore has no measurable effect on  $\delta^{18}\text{O}$  values in zircon (Valley et al., 1994). At magmatic temperatures, equilibrium values for  $\Delta(\text{Zrc-WR})$  range from  $\sim -0.5 \text{ ‰}$  for mafic rocks to  $\sim -2.0 \text{ ‰}$  for granites according to the relationship (Lackey, 2005; Valley et al., 1994, 2005):

$$\Delta^{18}\text{O}(\text{Zrc-WR}) = \delta^{18}\text{O}(\text{Zrc}) - \delta^{18}\text{O}(\text{WR}) \sim -0.0612 (\text{wt\% SiO}_2) + 2.5 \quad (1)$$

For the CnG diorite ( $\delta^{18}\text{O}(\text{WR}) = 7.2 \pm 0.4 \text{ ‰}$  ( $n=2$ );  $\text{SiO}_2(\text{WR}) = 54.6 \text{ wt\%}$ ;  $\delta^{18}\text{O}(\text{Zrc}) = 6.0 \pm 0.6 \text{ ‰}$ )  $\Delta(\text{Zrc-WR})$  values lie between  $-1.8 \text{ ‰}$  and  $-0.6 \text{ ‰}$  (taking the error on the analyses into account), which is in agreement with a calculated

equilibrium  $\Delta(\text{Zrc-WR})$  of -0.8. Thus, CnG zircons appear to be in isotopic equilibrium with their host rock (Fig. 6). Zircon crystals in the AD1 diorite ( $\delta^{18}\text{O}$  (WR) =  $7.0 \pm 0.4$  ‰ (n=2);  $\text{SiO}_2$  (WR) = 53.0 wt%;  $\delta^{18}\text{O}$  (Zrc) =  $7.1 \pm 0.4$  ‰) contain two apparent populations of oxygen isotope values that cannot both be in isotopic equilibrium with the host rock, and in themselves indicate isotopic disequilibrium.

A change in  $\delta^{18}\text{O}$  (zircon) can only be achieved by adding material of a different oxygen isotope composition to a magma (Valley, 2003), which implies that the two apparent  $\delta^{18}\text{O}$  populations in the AD1 zircons must represent mixing of at least two components. In most cases where zircon grains show resolvable variation in  $\delta^{18}\text{O}$  between different parts of the crystal, this is manifested as an increase in  $\delta^{18}\text{O}$  from core to rim reflecting mixing of a higher- $\delta^{18}\text{O}$  melt with the magma. However, the reverse trend has also been observed (grain 10), which suggests components less enriched in  $^{18}\text{O}$  were also mixed into the magma at some stage. We conclude that the two apparent populations do not represent simple mixing of only two components. Instead, a more complicated scenario is envisaged in which there were at least two melt batches (a high- $\delta^{18}\text{O}$  melt with  $\geq 8.1$  ‰ and a lower- $\delta^{18}\text{O}$  melt with  $\leq 6.6$  ‰ representing the highest and lowest measured zircon values (rim in grain 11 and c2 domain in grain 10, respectively)). Plausibly, multiple batches mixed with the magma *during* zircon growth. Imperfect mixing may also have led to some of the variation observed between zircon crystals. Due to this complicated mixing history we conclude that neither major zircon population in AD1 can have been in equilibrium with the present host rock. Independent textural or geochemical evidence for magma mixing has not been recognised in AD1.

The outer rims of zircon crystals are most likely to be in equilibrium with the current host rock. Comparing zircon rim and whole-rock  $\delta^{18}\text{O}$  data is complicated as zircon rims fall into low- $\delta^{18}\text{O}$  (6.1-6.5 ‰) (1 grain) and high- $\delta^{18}\text{O}$  (7.5-7.6 ‰) (5 grains) groups. Considering a calculated  $\Delta(\text{Zrc-WR})$  value of -0.7 ‰ (53.0 wt%  $\text{SiO}_2$ ) and the AD1 whole-rock composition of  $7.0 \pm 0.4$  ‰, only the low- $\delta^{18}\text{O}$  rims can be in isotopic equilibrium (Fig. 7). To be in equilibrium with the high- $\delta^{18}\text{O}$  rims, the whole-rock oxygen isotope composition would have to lie between 7.8 ‰ and 8.7 ‰, and as high- $\delta^{18}\text{O}$  rims appear to be more common they may be more

representative of the bulk magma from which the zircons crystallised. This would suggest that the current host rock underwent depletion in  $^{18}\text{O}$ , possibly by further mixing with low- $\delta^{18}\text{O}$  components, or by hydrothermal alteration, for example by interaction with heated meteoric water (Farver and Yund, 1991; Smith, 1981) after zircon had crystallised. Since plagioclase and biotite show only minor signs of alteration, any hydrothermal alteration would have occurred at or close to magmatic temperatures. The fact that zircons and whole-rock are in isotopic equilibrium in the CnG diorite suggests that it was unaffected by alteration even though the CnG and AD1 intrusions are located only approximately 1.5 km apart from each other. Hydrothermal fluids typically have heterogeneous flow paths, differing flow durations and fluid/rock ratios, and the intensity of alteration can vary at  $\mu\text{m}$  to km scales (Valley and Graham, 1996). Alternatively, isotopic equilibrium between zircon and whole-rock in the CnG diorite is fortuitous.

## 5.2. *Quartz – zircon equilibrium fractionation*

Quartz in granite is less susceptible to hydrothermal alteration than its whole-rock host, reflecting the susceptibility of feldspar to rapid isotopic exchange with hydrothermal fluid down to temperatures of 300-400°C. Quartz exchanges oxygen isotopes mainly by solution/re-precipitation and by slow temperature-dependent volume diffusion, exploiting fractures and crystal boundaries (Valley and Graham, 1996). Hence, if annealed cracks and obviously altered areas are avoided during analysis, the  $\delta^{18}\text{O}$  of zircon and quartz may provide a reliable indication of the state of isotopic equilibrium and of magmatic evolution.

In contrast to the zircon oxygen isotope data,  $\delta^{18}\text{O}$  (Qtz) analyses from both the CnG and AD1 diorites yield unimodal oxygen isotope populations (Fig. 6). Hence,  $\delta^{18}\text{O}$  (Qtz) in AD1 and CnG provide no evidence of magma mixing. Examining the equilibrium fractionation between zircon and quartz may potentially explain this phenomenon.

Equilibrium oxygen isotope fractionation factors between quartz and zircon ( $\Delta(\text{Qtz-Zrc})$ ) as a function of temperature are given by the empirical equation (Valley et al., 2003):

$$\delta^{18}\text{O}_{\text{Qtz}} - \delta^{18}\text{O}_{\text{Zrc}} = \Delta_{\text{Qtz-Zrc}} \approx 1000 \ln (\alpha_{\text{Qtz-Zrc}}) = A_{\text{Qtz-Zrc}} 10^6/T^2 \quad (2)$$

where  $A_{\text{Qtz-Zrc}} = 2.64 \text{ (}\% \text{K}^2\text{)}$ ;  $T$  = temperature in degrees Kelvin.

At 800°C the equilibrium value of  $\Delta(\text{Qtz-Zrc})$  is 2.3 ‰. However, for diorite CnG (mean  $\delta^{18}\text{O}(\text{Zrc}) = 6.0 \pm 0.6$ , mean  $\delta^{18}\text{O}(\text{Qtz}) = 10.9 \pm 0.5\%$ ) the calculated  $\Delta(\text{Qtz-Zrc})$  is  $4.9 \pm 1.1 \%$ . Due to the complex  $\delta^{18}\text{O}(\text{Zrc})$  distribution in AD1, the mean oxygen isotope value of zircon cannot be used for this calculation. Instead we use the lowest and highest measured zircon values ( $\delta^{18}\text{O}(\text{Zrc}) = 6.1\text{--}8.1 \pm 0.4 \%$ , mean  $\delta^{18}\text{O}(\text{Qtz}) = 11.7 \pm 0.6 \%$ ), yielding  $\Delta(\text{Qtz-Zrc})$  of  $5.6\text{--}3.6 \pm 1.0 \%$ . Taking the error into account, the  $\Delta(\text{Qtz-Zrc})$  value is at least 1.2 ‰ higher in CnG and 0.3 ‰ higher in AD1 than the calculated value of 2.3 ‰ for isotopic equilibrium at 800°C using equation (2). A temperature of 700°C would permit equilibrium between only the highest  $\delta^{18}\text{O}$ -zircons observed in the AD1 diorite and quartz (and only if the error is taken into account). We conclude that zircon and quartz are not in isotopic equilibrium.

Other authors (e.g. King and Valley, 2001; Monani and Valley, 2001) have found that quartz does not always preserve magmatic  $\delta^{18}\text{O}$  values as robustly as zircon, due to post-magmatic hydrothermal diffusive oxygen exchange and alteration. However, the lack of oxygen isotope heterogeneity along cracks and crystal boundaries or between different quartz crystal sizes in AD1 and CnG suggests that in both samples quartz has essentially retained its oxygen isotope composition from the time of crystallisation and therefore high  $\delta^{18}\text{O}(\text{Qtz})$  was not caused by hydrothermal alteration or closed-system exchange with feldspar. We conclude that in the CnG diorite quartz crystallised (or completely recrystallised) from late magmatic or high-temperature post-magmatic (subsolidus) fluids with high  $\delta^{18}\text{O}$  after zircon had ceased to crystallise. The analysed zircons may contain a very thin outer rim that is in equilibrium with quartz, but due to the spatial resolution of the ion microprobe this is not detectable. Quartz in AD1 also forms a homogeneous oxygen isotope population in contrast to co-existing zircon, and hence disequilibrium between quartz and zircon, and a similar may also be assumed.

In summary, both zircon and quartz in the Lochnagar diorites preserve their oxygen isotope compositions from the time of crystallisation. However, textural and isotopic evidence strongly suggests that zircon and quartz crystallised at different times, and hence we conclude that they represent different magma (or fluid) compositions. As oxygen isotope evidence of magma mixing was only found in AD1 zircons and not in quartz, the  $^{18}\text{O}/^{16}\text{O}$  of the AD1 magma (or late magmatic fluid) must have been completely homogenised and relatively more  $^{18}\text{O}$ -enriched at the stage of quartz crystallisation.

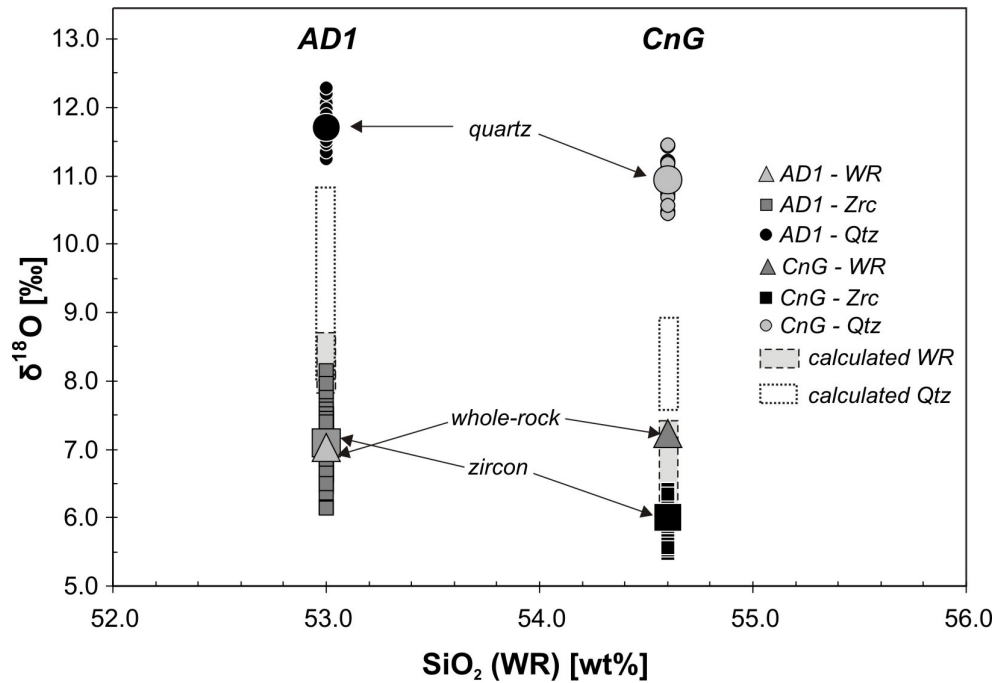


Fig. 7: Evaluation of equilibrium between zircon (Zrc), quartz (Qtz) and whole-rock (WR). 'Calculated WR' and 'calculated quartz' are calculated using equations (1) and (2) (see text); calculations include the error on the zircon analysis.

AD1: Zircon is not in equilibrium with quartz or whole-rock. Measured whole-rock is too low to be in equilibrium with zircon, which suggests it was affected by hydrothermal alteration after zircon crystallisation.

CnG: Zircon and quartz are not in equilibrium as measured quartz  $\delta^{18}\text{O}$  is considerably higher than the calculated quartz value, which suggests quartz crystallised late in sequence. Zircon and whole-rock are in equilibrium. Low modal percentage of elevated quartz in whole-rock (<5 %) did not shift whole-rock out of equilibrium.



### 5.3. Petrogenetic evolution model

The granites and diorites of the Lochnagar pluton belong to a suite of late Caledonian I-type intrusions in Scotland whose protoliths are thought to be “igneous” or “infracrystal” insofar as these protoliths have not experienced a weathering cycle (Chappell and Stephens, 1988). I-type granitic rocks are widely considered to be the products of either (1) (re)melting of deep-crustal igneous rocks, implying that they are the products of crustal differentiation and recycling rather than crustal growth; or (2) the interaction (by melting or assimilation) of mantle-derived (mafic) magmas with older crustal rocks, implying the generation and growth of new continental crust (e.g. Kemp and Hawkesworth, 2005).

Zircons in equilibrium with pristine mantle melts have  $\delta^{18}\text{O}$  of  $5.3 \pm 0.6 \text{ ‰}$  ( $2\sigma$ , Valley et al., 1998). This value is insensitive to modification by differentiation since whole-rock  $\delta^{18}\text{O}$  and  $\Delta(\text{melt} - \text{Zrc})$  increase in parallel as differentiation and accompanying increase of  $\text{SiO}_2$  proceed (Valley et al., 1994). The occurrence of zircons with  $\delta^{18}\text{O} > 5.6 \text{ ‰}$  in dioritic rocks thus indicates that the protoliths contained an  $^{18}\text{O}$ -enriched supracrustal component or an altered igneous source, and/or represent the interaction of mantle-derived magmas with supracrustal materials.

Zircon crystals in the Lochnagar diorites are enriched in  $^{18}\text{O}$  by an average of 0.7 ‰ to 2.1 ‰ relative to pristine mantle values ( $\delta^{18}\text{O}$  (CnG) =  $6.0 \pm 0.6 \text{ ‰}$ ;  $\delta^{18}\text{O}$  (AD1) =  $7.1 \pm 0.4 \text{ ‰}$ ), indicating the involvement of  $^{18}\text{O}$ -enriched crustal protoliths (supracrustal rocks or altered igneous rocks) in their generation or evolution, either as remelted protoliths or by assimilation or mixing of such protoliths in mantle-derived mafic magmas. Evidence for the involvement of mantle-derived melts may be preserved in zircon crystals with  $\delta^{18}\text{O} < 5.9 \text{ ‰}$  in the CnG diorites that overlap into the mantle field (Fig. 3). These may have crystallised early in the crystallisation history of the CnG diorite in order to capture evidence of a mantle component before any magma mixing processes took place similar to those recorded in diorite AD1. On a wider scale, mafic enclaves in granites and the occurrence of appinites, lamprophyres and rare gabbroic intrusions of late Caledonian (430-400 Ma) age indicate an indirect role for mantle-derived melts in the genesis of the late

Caledonian granites in Scotland (Strachan et al., 2002). However, the absence of any persuasive evidence of a pristine mantle source in the  $\delta^{18}\text{O}$  (Zrc) data for the Lochnagar diorites suggest an origin dominated by remelting of mafic lower crustal sources and crustal differentiation rather than crustal growth. On the other hand, the  $\delta^{18}\text{O}$  (Zrc) values are not strongly  $^{18}\text{O}$ -enriched, and a large supracrustal contribution by for example Dalradian Supergroup metasedimentary host rocks can therefore be ruled out.

Several models have been proposed for the origin of intermediate and silicic calc-alkaline magmas. These include fractional crystallisation of mantle-derived basalt or basaltic andesite in shallow crustal magma chambers (e.g. Grove et al., 1997; Pichavant et al., 2002; Sisson and Grove, 1993) or at/close to the Moho (e.g. Annen and Sparks, 2002; Mortazavi and Sparks, 2003; Müntener et al., 2001; Prouteau and Scaillet, 2003), and dehydration melting in lower or middle crust induced by intrusion of hot, hydrous, mafic, mantle-derived magma (e.g. Jackson et al., 2003; Petford and Atherton, 1996; Smith and Leeman, 1987). Based on numerical modelling and experimental data Annen and Sparks (2002) have proposed the existence of 'deep crustal hot zones' and have recently applied this model (Annen et al., 2006) to the generation of intermediate and silicic igneous rocks in subduction zone settings.

The development of deep crustal hot zones results from repeated intrusion of mantle-derived hydrous basalt sills into the lower crust, where melts are generated either by (1) differentiation of the basalt sills to produce residual and more siliceous  $\text{H}_2\text{O}$ -rich melts, or by (2) partial melting of pre-existing crustal rocks (including early basalt sills). Mixing of residual melts (or mafic mantle melts) and crustal partial melts creates a large range of intermediate and silicic melts with variably  $^{18}\text{O}$ -enriched compositions. The efficiency of melt production in deep crustal hot zones largely depends on the amount of intruding basalt, the level of emplacement in the crust, the rate of emplacement and the composition of the lower and middle crust. Residual melts are most efficiently produced by differentiation of basalt at deep crustal levels. In contrast, the largest amounts of crustal partial melts are generated either by random basalt sill injection over extended periods of time at different mid- and lower crustal levels, heating the crust from below and above, or by emplacement

of sills at the contact with a fertile upper crust. Thus, the basalt sills predominantly act as a heat source required for generation of crustal partial melts, but do not necessarily represent the dominant component in the generated melts. After melt generation, melts segregate and, depending on their H<sub>2</sub>O content, density, viscosity and ascent path, ascend more or less rapidly into shallow reservoirs in the upper crust where they undergo crystallisation by degassing and cooling (Annen et al., 2006).

The tectonic setting that led to intrusion of the late Caledonian 'I-type' magmatism in Scotland is still controversial. The late Caledonian granites have commonly been linked to a subduction zone setting (Brown, 1991; Brown et al., 1985; Soper, 1986; Stephens and Halliday, 1984; Stephenson et al., 1999; Thirlwall, 1981, 1982, 1988), and more recently a slab-breakoff model has been proposed (Atherton and Ghani, 2002). Based on the complexity of the zircon oxygen isotope data observed in the AD1 diorite magma generation in a 'deep crustal hot zone' may provide a suitable model to explain the generation of the Lochnagar diorites. As neither CnG nor AD1 diorites contain populations of zircons with pristine mantle  $\delta^{18}\text{O}$  signatures the diorites do not appear to have formed by simple closed-system fractional crystallisation of contemporaneous mantle-derived melts. Assimilation and fractional crystallisation may explain the zircon oxygen isotope composition of the CnG diorite. However, the observed increase and decrease in  $\delta^{18}\text{O}$  (zircon) with zircon growth in the AD1 diorite, which indicates mixing or assimilation of lower and higher  $\delta^{18}\text{O}$  materials, is inconsistent with this process. We therefore propose that the diorites formed in a deep crustal hot zone either by (1) mixing of residual melts and crustal partial melts, or by (2) partial melting of a mafic lower crust. Model 1 implies that zircons with mantle-like  $\delta^{18}\text{O}$  values represent a contemporary ~420 Ma mantle-derived component, hence new crust, whereas in model 2 mantle-like zircons reflect melting of old lower crust with a mantle-like composition, hence crustal differentiation. Based on oxygen isotope data alone it is not possible to distinguish between these two models, but due to the overall small number of mantle-like zircons crustal recycling appears to have been the dominant process.

Valuable information was also gained about the magmatic evolution of the dioritic magmas, which appear to differ significantly. The homogeneity in  $\delta^{18}\text{O}$  of the CnG zircons suggests they precipitated from a single homogeneous magma and

did not experience open-system processes during zircon growth. In contrast, the AD1 magma experienced *at least* two mixing events involving a high  $\delta^{18}\text{O}$  ( $\geq 8.1$  ‰) and a lower- $\delta^{18}\text{O}$  melt ( $\leq 6.6$  ‰). As these mixing events appear to have occurred during zircon growth, they probably took place at shallow crustal levels after ascent. The juxtaposition of two or more magmas of differing  $\delta^{18}\text{O}$  is consistent with a model of incremental assembly of melt batches in the AD diorite pluton. Resorption surfaces between cores and rims or between mantles do not appear to represent the timing of mixing as (1) a shift in  $\delta^{18}\text{O}$  between cores and rims was not always observed, (2) variations in  $\delta^{18}\text{O}$  exist within single zones, and (3) zircons from both the CnG and AD1 diorites contain resorption surfaces, but no evidence of mixing was found in CnG. Thus, these surfaces are more likely to represent local differences in the growth environment due to fluctuations in Zr content. In both diorites quartz crystallised late from homogenised, high- $\delta^{18}\text{O}$  melt or fluid, is thus not in equilibrium with zircon and shows no evidence of magma mixing. After zircon and quartz crystallisation, diorite AD1, and perhaps also the CnG diorite, may have been affected by high-temperature hydrothermal alteration by infiltration of hot meteoric fluids, resulting in a decrease in whole-rock oxygen isotope composition.

## 6. Conclusions

- 1) High-precision in-situ SIMS oxygen isotope analysis reveals small ( $\ll 1$  ‰) variations in oxygen isotope composition in zircon and quartz crystals in Scottish late Caledonian diorites at a spatial resolution of around 20  $\mu\text{m}$ .
- 2) Zircon in the Cul nan Gad diorite intrusion yields a unimodal distribution of oxygen isotope values with a mean of  $6.0 \pm 0.6$  ‰, whereas zircon in the Allt Darrarie diorite intrusion yields two apparent populations with means of  $6.6 \pm 0.4$  ‰, and  $7.4 \pm 0.4$  ‰. The  $\delta^{18}\text{O}$  composition of zircon preserved in growing crystals in the latter diorite can only evolve by open-system changes to the magma composition, so the presence of two populations of oxygen isotope values in zircon represents a cryptic record of magma mixing during zircon crystallisation. Detailed examination of the grain-scale variations reveals

increases as well as decreases in  $\delta^{18}\text{O}$  with zircon growth. This suggests that the two apparent populations do not represent simple mixing between two components, but indicates a more complicated process involving additional magma component(s).

- 3) Quartz oxygen isotope data show no evidence of a mixing event. Evaluation of  $\Delta(\text{Qtz-Zrc})$  values shows that quartz and zircon are not in equilibrium in either diorite host. This is interpreted to reflect quartz crystallisation late in the sequence, at lower temperatures and from a higher- $\delta^{18}\text{O}$  magma well after the mixing events in the Allt Darrarie magma.
- 4) Whole-rock and zircon oxygen isotope values appear to be in equilibrium in the Cul nan Gad diorite, although this may be fortuitous. In the Allt Darrarie diorite, the whole-rock  $\delta^{18}\text{O}$  value is too low, which indicates that it experienced further mixing or more likely hydrothermal alteration that did not affect either zircon or quartz.
- 5) The Lochnagar diorites are thought to have been generated in a 'deep crustal hot zone' by either (1) mixing of residual melts and crustal partial melts indicating that they incorporate new crust, or (2) melting of mafic lower crustal rocks, indicating crustal recycling. Based on oxygen isotope data alone it is not possible to distinguish between these two models, but the small number of zircons with mantle-like  $\delta^{18}\text{O}$  values is consistent with an origin dominated by crustal differentiation rather than crustal growth. A large supracrustal contribution can be ruled out.
- 6) Zircons from the Cul nan Gad diorite crystallised from a homogeneous melt; its magma did not experience open-system changes during zircon growth. Allt Darrarie diorite zircons experienced at least two mixing events during zircon growth.
- 7) A combined zircon, quartz and whole-rock oxygen isotope approach is a powerful way to constrain the petrogenetic evolution of plutons from early crystallisation to late alteration. However, only high-precision in-situ ion microprobe analysis of zircon is capable of revealing the cryptic record of multiple magma mixing events observed in the Allt Darrarie diorite.

# **III.**

## **PAPER 2**

**A tale of two plutons: an integrated ion  
microprobe study of  $^{18}\text{O}/^{16}\text{O}$ , U-Pb, trace  
elements and REE in zircons from Scottish  
Caledonian granites**

# A tale of two plutons: an integrated ion microprobe study of $^{18}\text{O}/^{16}\text{O}$ , U-Pb, trace elements and REE in zircons from Scottish Caledonian granites

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## Abstract

Integrating in-situ SIMS U-Pb, oxygen isotope, trace element and REE analyses of zircons provides the opportunity to access grain-scale information that cannot be detected by conventional techniques in order to decipher the petrogenetic histories of granitic plutons. We have used this approach to study zircons from two Scottish late Caledonian (c. 430-400 Ma) ‘I-type’ granites, the Lochnagar and Etive plutons. The plutons show large differences in their whole-rock trace element compositions, which have been interpreted to reflect either compositional variations in their sources or variations in the relative contributions of different sources (e.g. mantle vs. crust).

U-Pb dating has revealed that the emplacement histories of both plutons are more protracted and complicated than previously recognised, with magmatic activity at the Lochnagar pluton lasting for c. 11 m.y. (424-413 Ma) and at the Etive pluton for c.

16 m.y. (423-407 Ma). Oxygen isotope analyses of zircons show that the plutons comprise samples with both homogeneous and heterogeneous distributions of  $\delta^{18}\text{O}$ . In heterogeneous samples, resolvable variations occur both between zircon crystals within a single sample and within individual crystals (e.g. between cores and rims). Commonly, both decreases and increases in  $\delta^{18}\text{O}$  with zircon growth were observed, providing evidence for magma mixing. This scale and degree of this heterogeneity has not previously been reported.

The majority of zircon crystals (c. 80 %) are enriched in  $^{18}\text{O}$  relative to zircons with mantle-like  $\delta^{18}\text{O}$  values ( $5.3 \pm 0.6 \text{ ‰}$  ( $2\sigma$ )). This suggests that the plutons contain only a small pristine mantle component, are either derived from a mixture of mantle-derived and crustal materials or solely from infracrustal sources. Simple two-component magma mixing between mantle-derived melts and a supracrustal component, e.g. the Dalradian Supergroup country rocks, can account for the range of zircon  $\delta^{18}\text{O}$  values found in the Lochnagar and Etive plutons. However, the observed variation in zircon oxygen isotope composition indicates a more complex mixing/assimilation scenario involving several sources, which cannot be identified based on oxygen isotope data alone. In addition, it is impossible to decipher whether zircons with mantle-like  $\delta^{18}\text{O}$  values reflect a contribution by contemporary depleted and/or enriched mantle or actually represent pre-existing mafic lower crust. Minor inheritance of pre-magmatic zircon indicates a supracrustal component, most likely Dalradian Supergroup country rocks.

The large variation in  $\delta^{18}\text{O}$  measured in zircons from the Lochnagar and Etive pluton is attributed to a ‘deep crustal hot zone’ where mantle melts differentiated, inducing partial melting of the lower/middle crust and extensive mixing of melts with differing  $\delta^{18}\text{O}$ . Further mixing occurred during zircon growth during ascent and at shallower levels. Magmas were subsequently emplaced incrementally in small batches over extended periods of time. The processes and the relative contributions of mantle and crust involved in the genesis of the Lochnagar and Etive plutons were very similar. Thus, the whole-rock differences must be attributed to compositional differences between the sources.



## 1. Introduction

Due to the complexity and diversity of granitic rocks, and the difficulty of recognising unambiguous geochemical and petrological signatures of their sources, their petrogenesis and magmatic evolution have remained controversial. Following the classic study of Chappell and White (1974) on the origin of the granitic rocks of the Lachlan Fold Belt, southeastern Australia, plutons have been widely considered to have either igneous (infracrystal) or sedimentary (supracrystal) precursors, which may be distinguished by their whole-rock chemistry. However, more recent studies have demonstrated that granites rarely have a single source, but commonly represent complicated mixtures of melts derived from the mantle and from infra- and/or supracrystal sources (John and Wooden, 1990; Kemp et al., 2007; Kemp and Hawkesworth, 2003; Miller et al., 1990). The relative proportions of mantle and crustal contributions in the voluminous I-type granites that characterise collision belts and volcanic arcs have key significance for the role of granite genesis in the growth and differentiation of the Earth's continental crust (e.g. Hawkesworth and Kemp, 2006a; Kemp et al., 2007).

Recent advances in in-situ microanalysis permit the study of granites using the geochemical record stored in zircon. Due to its refractory nature, zircon retains information about its parental melt(s). Changes in melt composition, temperature or crystallisation conditions with time arising from either local closed-system processes or large-scale open-system changes (e.g. magma mixing, assimilation) are recorded in zircon growth zones (Hoskin and Schaltegger, 2003; Shore and Fowler, 1996; Vavra, 1990, 1993, 1994), which may be imaged by cathodoluminescence (CL) and back-scatter electron (BSE) imaging techniques. With significant concentrations of U, Th and REEs (ppm level) (Kinny and Maas, 2003), zircon is suitable for oxygen isotope, U-Pb and trace element/REE analysis. Due to the high spatial resolution of the ion microprobe, multiple analyses may be made within a single zircon grain, which permits correlation of elemental and isotopic changes with zircon growth (e.g. changes between zircon cores and rims). Furthermore, oxygen, U-Pb and REE analyses may now be carried out on the same c. 20  $\mu\text{m}$  spot, which enables direct spatial correlation to be made between the different data sets. This approach may be

used to constrain the emplacement ages of plutons (U-Pb data), and their sources (mantle, infracrustal and/or supracrustal) (O and REE data), and to resolve processes such as magma mixing (Paper 1).

In this paper we apply these integrated techniques to zircons from the Lochnagar and Etive plutons, which are representative of the Scottish late Caledonian (c. 430-400 Ma) I-type granites, in order to constrain their emplacement histories, and to assess the role of mantle, infracrustal and supracrustal sources in the genesis of this classic and voluminous suite of I-type granites.

## **2. The late Caledonian granites**

The Caledonian I- and S-type granites represent a classic granite suite that is mostly located in the Grampian Highlands of Scotland. The main focus of previous research has been the late Caledonian calc-alkaline I-type granites, which were emplaced into Dalradian metasediments in the Grampian Highlands between c. 430 Ma and 400 Ma (Fig. 1) (Oliver, 2001; Rogers and Dunning, 1991; Stewart et al., 2001). The main phase of emplacement, between 425 and 430 Ma (Oliver, 2001), was broadly contemporaneous with - and subsequent to - the Scandian event, which involved the oblique collision of Baltica and Laurentia (Brown et al., 1985; Brown, 1991; Coward, 1990; Dallmeyer et al., 2001; Dewey and Mange, 1999; Kinny et al., 2003; Soper, 1986; Stephens and Halliday, 1984; Stephenson et al., 1999; Thirlwall, 1981, 1982, 1988). However, the connection between the collision and the voluminous I-type magmatism is unclear.

The Caledonian I-type plutons have geochemical features typical of modern continental arcs with the majority showing a metaluminous affinity (except for granites with > 70 wt% SiO<sub>2</sub>, which are peraluminous) (Frost et al., 2001). They are commonly hornblende-bearing (Soper, 1986) and contain high Rb/Sr and K/Na, low K/Rb and relatively low initial Sr isotope ratios (Halliday et al., 1985; Stephens, 1988; Thirlwall, 1988). Their origin has previously been linked to a subduction zone setting (Brown, 1991; Brown et al., 1985; Soper, 1986; Stephens and Halliday, 1984; Stephenson et al., 1999; Thirlwall, 1981, 1982, 1988), but more recently a slab-

breakoff model has been proposed (Atherton and Ghani, 2002). However, the exact tectonic setting that led to emplacement of the late Caledonian I-type granites in Scotland is still controversial.

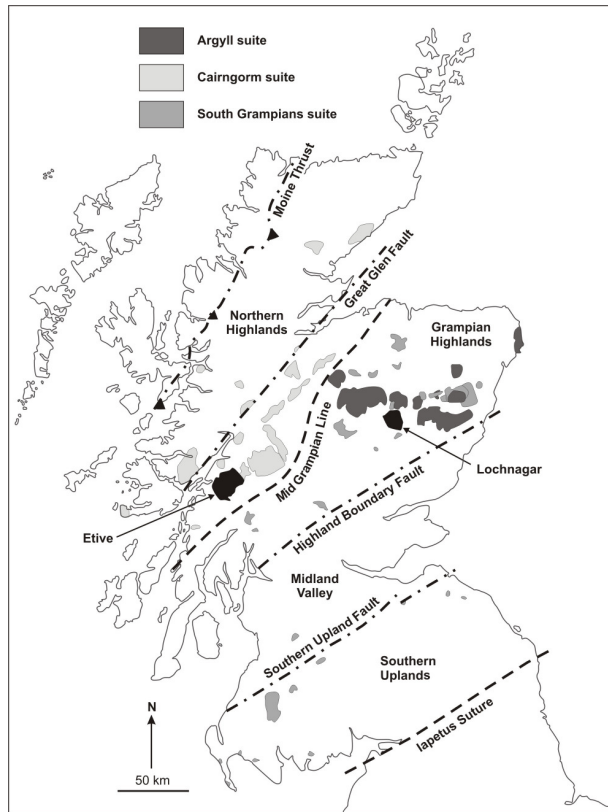


Fig. 1: Map of the late Caledonian granites (after Stephenson et al., 1999).

On the basis of whole-rock geochemical and isotopic data three late Caledonian I-type granite suites - the Argyll, Cairngorm and South Grampians suites - have been distinguished (Fig. 1) (Stephens and Halliday, 1984). The *Argyll suite* consists of hornblende-biotite granodiorite and biotite granodiorite plutons with minor dioritic, appinitic and monzogranitic components (Stephen and Halliday, 1984; Strachan et al., 2002). The plutons are strongly metaluminous and are enriched in Ba, Sr and Na relative to the plutons of the other suites, whereas Nb, Th and Rb are present only at low concentrations (Fowler et al., 2001; Halliday, 1984; Halliday et al., 1985; Stephens and Halliday, 1984; Tarney and Jones, 1994; Thirlwall, 1988). The *Cairngorm suite* consists of biotite monzogranite with minor granodiorite, which

varies texturally between microgranite and coarse-grained, K-feldspar megacrystic granite. The intrusions contain high concentrations of Rb, Nb, Th and U, but have low Ba, Sr, Ti, P contents (Stephens and Halliday, 1984). The *South Grampians suite* is dominated by granodiorites and monzogranites, and has a higher proportion of gabbroic and appinitic intrusions. In general, this suite is strongly metaluminous with higher K and Th abundances than the Argyll suite, but lower concentrations of Zr, La, Ce, Ba and Rb (Stephenson et al., 1999).

To date the compositional differences between the suites are not fully understood; they may reflect heterogeneities in the composition and age of the underlying lower crustal basement and/or mantle, or differences in the relative mantle and crustal contributions. Halliday et al. (1984) proposed the existence of the Mid Grampian Line (MGL) separating the Argyll suite plutons in the northwest from the Cairngorm and South Grampians suite plutons in the southeast, which may represent an important boundary in the deep basement and possibly in the mantle.

### **3. Methodology**

#### *3.1. Whole-rock analysis*

Major and trace elements were determined at the University of Edinburgh using a PW2404 wavelength-dispersive sequential X-ray spectrometer. Rare earth elements (REEs) and some trace elements (Y, Hf, Th, U) were analysed at the British Geological Survey (BGS) in Nottingham. The samples were fused with Na<sub>2</sub>O<sub>2</sub> and then leached with deionised water and HCl before analysis by ThermoElemental PQ Excel quadrupole ICP-MS. Matrix-matched standards were used throughout (data are presented in Appendix 2a).

#### *3.2. Zircon sample preparation*

Zircon separation was carried out at the University of St. Andrews Mineral Separation Facility. Rock samples of approximately 5 kg were crushed and sieved to

obtain the < 500  $\mu\text{m}$  fraction from which zircon crystals were separated using a Wilfley Table, heavy liquids and a Frantz magnetic separator. Approximately 100 zircon crystals were hand-picked from the remaining heavy, non-magnetic fraction, providing a range of grain sizes, morphologies, degrees of transparency, alteration and occurrence of inclusions or cracks. The crystals were mounted in epoxy (Araldite/Epothin) along with fragments of the “91500” and “Temora 2” zircon standards. Subsequently, the zircon mounts were polished to about half thickness to expose the crystal interiors. The polished surfaces were imaged in back-scattered electron (BSE) and cathodoluminescence (CL) mode using a Philips XL30CP Scanning Electron Microscope (SEM) at the University of Edinburgh to identify internal zoning features, inherited material, inclusions and cracks. Suitable crystals for in-situ oxygen isotope analysis were selected based on this grain characterisation.

### *3.3. Zircon oxygen isotope analysis*

Zircon oxygen isotope data were obtained using a Cameca ims-1270 ion microprobe at the University of Edinburgh following the methods of Cavosie et al. (2005) and Kemp et al. (2006). A 6nA primary  $^{133}\text{Cs}^+$  ion beam with a diameter of c. 20  $\mu\text{m}$  was used, charge was neutralised using a normal-incidence electron flood gun, secondary ions were extracted at 10 kV, and  $^{18}\text{O}^-$  and  $^{16}\text{O}^-$  ions were monitored simultaneously on dual Faraday cups. Secondary ion beam centring, pre-sputtering for 50 seconds and subsequent data collection over 10 cycles (total counting time: 40 seconds = 4 seconds per cycle) resulted in a total acquisition time of c. 200 seconds. The secondary yield of  $^{18}\text{O}$  under these conditions was typically between  $4.5 \times 10^6$  and  $5.5 \times 10^6$  counts per second. To correct for instrumental mass fractionation (IMF) and instrumental drift, all data were normalised to zircon standard 91500 ( $\delta^{18}\text{O} = 9.86 \text{‰}$ ) (Wiedenbeck et al., 2004), which was analysed in blocks of 5 to 10 after every 10 to 15 unknown zircon analyses. During stable instrument conditions the unknown zircon analyses were normalised to the daily average  $^{18}\text{O}/^{16}\text{O}$  value obtained for 91500. In cases where instrumental drift was recognised, the analytical conditions changed or sample exchange was carried out, the data were divided into

sessions in which unknowns were normalised to the linearly interpolated  $^{18}\text{O}/^{16}\text{O}$  value derived from analyses of the bracketing 91500 standard.

Prior to oxygen isotope analysis,  $\text{HfO}_2$  concentrations in the zircons were measured by electron microprobe as variations in  $\text{HfO}_2$  have been shown to cause variations in IMF (Peck et al., 2001). This has been shown to be particularly important when conducting analysis using e.g. a Cameca ims-4f at high-energy offset. However, in this study oxygen isotope analysis were carried out using a Cameca ims-1270 ion microprobe, and in both diorite samples  $\text{HfO}_2$  variations in zircons were  $\leq 0.5$  wt %; therefore corrections for IMF were unnecessary. The internal precision of individual point analyses based on counting statistics varied between 0.1-0.4 ‰ (1SD). External precision based on the reproducibility of standard 91500 ranged from 0.2-0.7 ‰ and 0.031 to 0.145 (1 s.e.m.).

Analyses were conducted in clear, crack- and inclusion-free areas on representative zircon crystals. Where possible, multiple analyses (core to rim) were carried out on single zircon crystals to collect information about the zircon growth history, and occasionally also in adjacent spots within crystals to assess reproducibility. The ion probe pits were subsequently imaged in BSE and Secondary Electron (SE) mode using an SEM to determine the exact position of the analyses and to ensure that no cracks in the bottom of pits might have influenced the results. Data obtained from suspect locations were rejected. Furthermore, since metamict zircon grains generally have lighter  $\delta^{18}\text{O}$  values than non-metamict crystals (Booth et al. 2005; Valley et al. 1994), all data obtained from areas of crystals showing  $\geq 20$  % discordance were also excluded. In addition, data were rejected when the correction on the position of the secondary ion beam was anomalously large (summarised data are presented in Tables 2 and 4 and full data set in Appendices 2b and 2e).

### *3.4. U-Th-Pb analysis*

Subsequent to oxygen isotope analysis, U-Th-Pb analyses were carried out also using the Cameca ims-1270 at the EIMF. Analytical procedures are similar to those described by Schuhmacher et al. (1994) and Whitehouse et al. (1997), and are described in detail in Kelly et al. (accepted). Zircons were analysed using a  $\sim 4\text{nA O}_2^-$

primary ion source with 22.5 keV net impact energy. The beam was focused using Köhler illumination, with primary beam alignment giving ellipsoidal analysis pits (~25  $\mu\text{m}$  max. dimension). Spatial resolution of the analysed area was further limited by the use of the field aperture. U, Th and Pb were analysed at a mass resolution ( $M/\Delta M$ ) of ~4000R using a peak switching routine. An energy window of 60 eV was used throughout, with energy centring on each analysis using the HfO peak. Oxygen flooding on the surface of the sample was employed to enhance Pb ion yields. Prior to analysis the sample surface was pre-rastered over an area of ~40  $\mu\text{m}$  for 120 seconds to remove any surface contamination.

Calibration of Pb/U ratios followed procedures employed by other SHRIMP and/or Cameca ims-1270 laboratories and were based on the observed relationship between Pb/U and ratios of UO/U (e.g. Claoué-Long et al., 1995; Compston et al., 1984; Schuhmacher et al., 1994; Williams, 1998; Williams and Claesson, 1987; Whitehouse et al., 1997). However, the relationship  $\ln(\text{Pb}/\text{U})$  vs.  $\ln(\text{UO}_2/\text{UO})$  was found to give a better within-session reproducibility than the conventional  $\ln(\text{Pb}/\text{U})$  vs.  $\ln(\text{UO}/\text{U})$  or  $\ln(\text{Pb}/\text{U})$  vs.  $\ln(\text{UO}_2/\text{U})$  methods.

U/Pb ratios were calibrated against measurements on standard 91500 (Wiedenbeck et al., 1995: ~1062.5 Ma; assumed  $^{206}\text{Pb}/^{238}\text{U}$  ratio = 0.17917), which is measured after 3-4 unknowns. Temora 2 was analysed as a secondary standard after every 10-15 analyses. Th/U ratios in unknowns were calculated by reference to measurements of Th/U and  $^{208}\text{Pb}/^{206}\text{Pb}$  on the 91500 standard (Th/U = 0.362), assuming closed system behaviour. Elemental concentrations were determined based on the observed oxide ratios of the standard ( $\text{UO}_2/\text{Zr}_2\text{O}_2$  and  $\text{HfO}/\text{Zr}_2\text{O}_2$ ; assuming U = 81.2 ppm, Hf = 5880 ppm).

Corrections were carried out for dead time, detector background (~0.025 counts/second) and common Pb. Common Pb corrections were made using the measured  $^{204}\text{Pb}$  counts above detector background and the modern day composition of common Pb. Typically  $^{204}\text{Pb}$  count rates approached those of the background, which led to corrections of < 15 ppb on  $^{206}\text{Pb}$ .

Uncertainties on the Pb/U ratios include an error based on observed uncertainty from each measured ratio, which is generally close to that expected from counting statistics. Observed uncertainties on the U/Pb ratio of 91500 are generally an

additional 0.3% in excess of that expected from counting statistics alone. This is assumed to be a random error (see also Ireland and Williams, 2003) and has been propagated (in both standards and unknowns) together with the observed variation in Pb/U ratios measured for each analysis (typically close to the counting errors). For measurement of the 91500 standard, uncertainties are typically between 0.7-1.0 % per analysis. Uncertainties on  $^{207}\text{Pb}/^{206}\text{Pb}$  ratios are based on observed variations from cycle to cycle during each analysis and commonly approach those expected from counting statistics. Uncertainties on ages quoted in the text and in tables for *individual analyses* (ratios and ages) are at the  $1\sigma$  level. All uncertainties in calculated *group* ages are reported at  $2\sigma$  level or 95 % confidence.

Plots and age calculations have been made using the computer program ISOPLOT/EX v3 (Ludwig, 2003). Ages of magmatic grains are presented as weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  average ages and include only concordant data points; ages of inherited grains (> 1000 Ma) are  $^{207}\text{Pb}/^{206}\text{Pb}$  ages. Following analysis, the ion probe pits were imaged in BSE and SE mode to check for inclusions and cracks in the bottom of the pit; where either one was accidentally analysed data were rejected. During data processing we noticed that zircons with high U concentrations (>1000 ppm) commonly give older ages or lie off Concordia. Electron back-scatter diffractometry (EBSD) of these zircons showed disturbance and even complete destruction of their crystal structure. To provide a robust data set we excluded all data obtained from zircons showing above 1000 ppm U. In addition, zircons displaying high common Pb concentrations and/or > 10 % discordance were also rejected (summarised data are presented in Tables 2 and 4; full data sets in Appendices 2c and 2f).

### 3.5. Zircon REE/trace element analysis

Trace element and REE concentrations were analysed on the Cameca ims-4f at the EIMF. Analytical and correction procedures followed those described by Hinton and Upton (1991). Zircons were analysed using a 14.5 keV primary beam of  $\text{O}^-$  at ~5nA primary current, with secondary ions measured at ~120 V offset. Due to relatively low REE abundances in zircon, 10 cycles were made through the selected



masses. Analyses were standardised against NIST SRM-610 glass standard and concentrations were referenced against Si. Zircon standard 91500 was used as a secondary standard. Elements analysed were Si, P, Ca, Ti, Sr, Y, Nb, Zr, Ba, Hf and the REE. Corrections were made for  $\text{ZrSiO}^+$  overlap on  $^{138}\text{Ba}^+$ ,  $^{139}\text{La}^+$ ,  $^{140}\text{Ce}^+$  and  $^{141}\text{Pr}^+$  using count rates measured at mass 134. The interference of LREE on HREE and  $\text{Hf}^{2+}$  on Y were corrected based on analysis of zircon standard 91500 (summarised data are presented in Tables 2 and 4, full data sets in Appendices 2d and 3g).

#### **4. The Lochnagar pluton**

The Lochnagar pluton, which is representative of the Cairngorm suite, crops out in the surrounding Dalradian metasediments over an area of c. 150 km<sup>2</sup>, and comprises three main granite facies (L1, L2, L3), microgranites and several marginal diorites (Fig. 2) (Smith et al., 2001). *L1*, which represents the oldest part of the pluton, is a predominantly coarse-grained and porphyritic circular pluton with a diameter of c. 15 km. It has been found in sharp contact with a coarse-grained but inequigranular variant, which has been interpreted to indicate a separate intrusive pulse of L1 (Smith et al., 2001).

*L2*, an oval intrusion (dimensions 12 x 9 km) that intruded L1, comprises mostly medium- to coarse-grained, inequigranular, unfoliated grey and pink leucocratic rocks. However, Oldershaw (1974) also reported several variants of L2, between which no sharp contacts were discovered, that range from inequigranular to porphyritic and may represent separate intrusive pulses. Both L1 and L2 granites were subsequently intruded by several pink quartz-K-feldspar-plagioclase-phyric microgranites, which are compositionally similar to their host granites (Smith et al., 2001).

*L3* granites are predominantly pink (also white) equigranular leucocratic biotite granites, which can be found in various locations within L1. As their contacts with L2 are not exposed, their relation is unclear. Compositionally the L3 granites are

more evolved than L1 and L2, hence may not be related to the main granite body (Smith et al., 2001).

The marginal *diorites* (dimensions: 4-5 x 1.8 km (Cul nan Gad diorite) and 0.6 x 0.4 km (Allt Darrarie diorite)) mostly consist of medium-grained, sometimes foliated, inequigranular quartz diorites. They are interpreted to be separate intrusive bodies that are related, but based on cross-cutting relationships older than the granite (Smith et al., 2001) (for a more detailed description of the petrography and field relationships see Table 1).

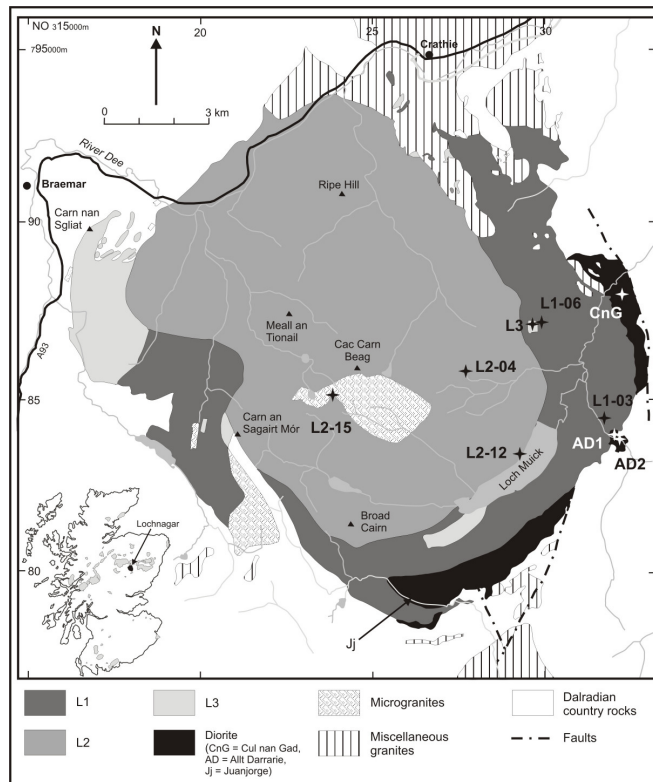


Fig. 2: Geological sketch map of the Lochnagar pluton with sample locations (Smith et al., 2001).

In summary, based on field relationships the order of pluton emplacement is (oldest to youngest) diorites, L1, L2, microgranite, L3 (Halliday, 1984; Halliday et al., 1979; Oldershaw, 1974; Smith et al., 2001). This order is supported by TIMS age data, which indicate that L1 and L2 were emplaced at c.  $425 \pm 5$  Ma (U-Pb zircon) and L3 some time later at c.  $417 \pm 1$  Ma (monazite age) (Smith et al., 2001).

**Table 1**  
**Summary of published petrographic and field relationship data of the Lochnagar pluton**

	<b>lithology</b>	<b>colour</b>	<b>grain size</b>	<b>texture</b>	<b>major phases</b>	<b>accessory phases</b>	<b>field relationships</b>
<b>Lochnagar</b>							
<b>L1</b>	granite	grey and pink	coarse-grained	mostly Kspar-phyrlic (up to 15 mm), can be inequigranular	plag (39%), Kspar (28%), qtz (23%), bt (8%), hbl (1%)	titanite, opaques, apatite, zircon	sharp contact between variants; cuts diorites
<b>L2</b>	granite	grey and pink	medium- to coarse-grained	inequigranular, may grade into Kspar-phyrlic; qtz clusters, isolated bt flakes	plag (41%), qtz (29%), Kspar (26%), bt (4%)	titanite, opaques, apatite, zircon	
<b>L3</b>	granite	pink	medium- to coarse-grained	equigranular	Kspar (40%), plag (33%), qtz (25%), bt (2%)	titanite, opaques, apatite, zircon	5 separate locations, intrudes L1, relation with L2 unknown
<b>Alt Darrarie diorite</b>	qtz diorite	dark grey	medium-grained	inequigranular, in places foliated, plag-phyrlic, clusters of hbl	plag, hbl, relic pyx, bt, qtz, Kspar		cut by L1, contains country rock xenoliths
<b>Cul nan Gad diorite</b>	qtz diorite, small area of granodiorite	dark grey	medium-grained	inequigranular, in places foliated, plag-phyrlic, clusters of hbl	plag (38%), hbl+relict pyx (38%), bt (6%), qtz (10%), Kspar (7%)	titanite, opaques, apatite, zircon	cut by L1, contains country rock xenoliths
<b>microgranites</b>	granite	pink	fine-grained	Kspar-plag-phyrlic	qtz (45%), Kspar (26%), plag (27%), bt (1%)	muscovite, titanite, opaques, apatite, zircon	cut L1, L2, L3

data from Oldershaw (1974) and Smith et al. (2001)

Nd and Sr isotope data for the Lochnagar pluton are scarce. However, Halliday et al. (1984) reported one  $\epsilon\text{Nd}_{415 \text{ Ma}}$  value of -2.7 and one initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of 0.7063 (n=1), and Halliday et al. (1979) an average initial  $^{87}\text{Sr}/^{86}\text{Sr}$  value of 0.7065 (n=5), which led to the interpretation that the pluton comprises both mantle and crustal sources.

#### *4.1. Samples*

Nine samples representing the main granite phases L1 (L1-03, L1-06), L2 (L2-04, L2-12, L2-15), L3, and the Allt Darrarie (AD1, AD2) and Cul nan Gad (CnG) diorites were chosen for analysis. Most samples vary texturally and/or compositionally from the published data to some extent (see Table 1) and also from each other when sampled from the same facies. For example, L1-03 is overall a typical K-feldspar-phyric L1 granite, but lacks hornblende. L1-06 is inequigranular to weakly porphyritic and contains less biotite (< 5 %). According to the literature, L2 comprises c. 40 % plagioclase, but sample L2-04 consists of equal amounts of K-feldspar, plagioclase and quartz (each c. 30 %) and c. 10 % biotite, and L2-12 and L2-15 are dominated by K-feldspar (40-45 %) and quartz (30-35 %) with less plagioclase (15-20 %) and biotite ( $\leq 5$  %). In addition, L2-04 and L2-12 contain euhedral allanite, which has not been reported before. On a microscopic scale L2-15 contains a 5 x 2 mm large, fine-grained (c. 0.5 mm) equigranular cluster of either restitic or entrained material, which comprises equal amounts of quartz, biotite, plagioclase and opaques (ilmenite and magnetite). The selected L3 sample is similar to the published data apart from the absence of accessory titanite. The proportion of mafic to felsic minerals in the three diorite samples (Allt Darrarie diorite = AD1, AD2; Cul nan Gad diorite = CnG) is as published, but the assemblage of the mafic minerals is very different. Diorites described in the literature contain c. 40 % hornblende plus relict pyroxene and 6 % biotite, whereas these samples contain 35-40 % biotite and  $\leq 10$  % hornblende.

#### 4.2. Zircon morphologies

Zircon crystals are euhedral and show oscillatory and/or sector zoning (Fig. 3a) typical of igneous zircon (Benisek and Finger, 1993; Hanchar and Miller, 1993; Hoskin and Schaltegger, 2003; Vavra, 1990). In each Lochnagar sample a range of sizes, morphologies and internal zoning textures were observed, which is a common phenomenon generally interpreted to be the result of varying local kinetic factors such as diffusion rates and adsorption (Dowty, 1980; Vavra, 1990, 1993). Zircon grain sizes vary between c. 200  $\mu\text{m}$  and  $\geq 700 \mu\text{m}$  along the c-axis with a higher abundance of elongated grains occurring in the diorites. With respect to internal zoning, all zircons consist of a core, which often defines most of the crystal, one or more rims. Cores and rims are separated by resorption surfaces, which are usually interpreted to reflect periods of Zr undersaturation in the magma for which the dominant controls are either large-scale mixing events or local kinetic phenomena (Corfu et al., 2003). Cores are either completely unzoned (c1) (Fig. 3b), comprise a relatively large unzoned inner domain (c1) and a surrounding outer oscillatory zoned domain (c2) (Fig. 3c) or appear to be entirely zoned (c2) (Fig. 3d). In terms of CL intensity, inner core domains are always moderately to weakly luminescent, whereas zones within the oscillatory-zoned domains vary between strongly and weakly luminescent. Rims consist of either a single or multiple zones, which may vary in CL intensity.

One striking difference was observed between samples L1-06, L2-12 and the remaining Lochnagar granite and diorite samples. Despite representing L1 and L2, respectively, samples L1-06 and L2-12 each comprise a very similar-looking homogeneous population of zircons, which display weak luminescence (Fig. 3e). The grains also contain cores and rims. These are commonly separated by a thin and more strongly luminescent resorption surface. Similar looking grains were not observed in any of the other Lochnagar granite or diorite samples.

Inherited zircon cores were found only in L2 samples L2-04 (n=1) and L2-15 (n=6). Some were easily identifiable as pre-magmatic cores with magmatic rims (Fig 3f), whereas others differed only slightly from the magmatic grains (Fig. 3g) and were only detected during U-Pb age dating.

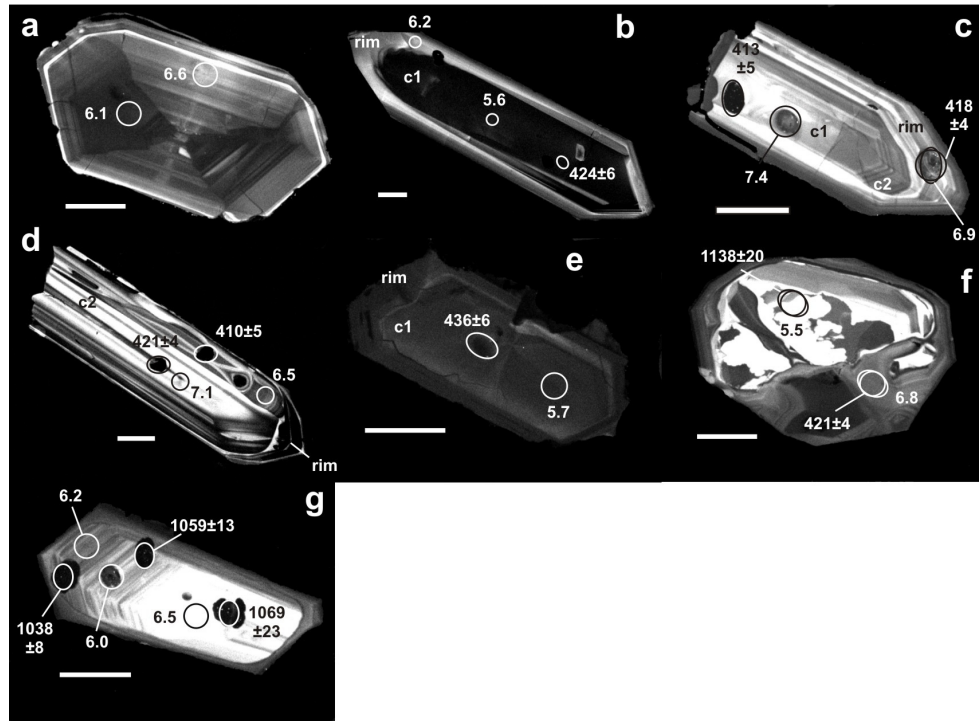


Fig. 3: CL images of representative zircons from the Lochnagar pluton with correlating  $\delta^{18}\text{O}$  values and U-Pb ages.

a) Sector zoning observed in L1, L2 and L3 zircons (grain 23, L1-03).

b) Elongated zircon crystal with resorbed weakly luminescent core (c1) and moderately luminescent rim (grain 15, CnG diorite).

c) Zircon with moderately luminescent, unzoned inner core domain (c1), outer oscillatory zoned domain (c2) and surrounding rim (grain 11, L2-04).

d) Zoned zircon core (c2) with surrounding rim (grain 13, AD2 diorite).

e) Weakly luminescent zircon typical of L1-06 and L2-12. Weakly luminescent core (c1) shows resorption surface (stronger luminescent) and is mantled by very weakly luminescent rim (grain 36, L2-06).

f) Inherited grain (grain 29) from L2-15. Grain consists of large pre-magmatic core and outer magmatic rim.

g) Inherited grain from L2-04 (grain 15). Grain is indistinguishable from magmatic zircons.

(Scale bar = 50  $\mu\text{m}$ ; circles indicate oxygen isotope analyses; ovals U-Pb analyses; quoted U-Pb error =  $1\sigma$ ,  $\delta^{18}\text{O}$  error = 0.5-0.7 ( $2\sigma$ )).

#### 4.3. U-Pb data

Sample L2-04 represents the oldest phase of the Lochnagar pluton with a weighted average age of  $424 \pm 5$  Ma. All remaining samples, with the exception of diorite AD2, give similar  $^{206}\text{Pb}/^{238}\text{U}$  ages that lie within  $2\sigma$  error of each other, ranging from  $423 \pm 2$  Ma for L3 to  $422 \pm 2$  Ma for L2-15,  $420 \pm 2$  Ma for L1-03,  $420 \pm 4$  Ma for L1-06,  $419 \pm 4$  Ma for L2-12,  $419 \pm 2$  Ma for diorite AD1 and  $418 \pm 3$

Ma for diorite CnG. However, diorite AD2 is younger at  $413 \pm 4$  Ma. Thus, the pluton intruded over a period of c. 11 m.y. (Fig. 4 & 5).

Inherited older material was found only in L2 (L2-04 and L2-15). L2-04 contains one inherited grain (out of 11 analysed grains), which has a  $^{207}\text{Pb}/^{206}\text{Pb}$  age of  $1046 \pm 33$  Ma. L2-15 comprises six grains (out of 16 analysed grains), which fall into three age groups; analyses are weakly discordant and yield  $^{207}\text{Pb}/^{206}\text{Pb}$  ages of  $1149 \pm 18$  Ma,  $1235 \pm 45$  Ma and  $1397 \pm 9$  Ma.

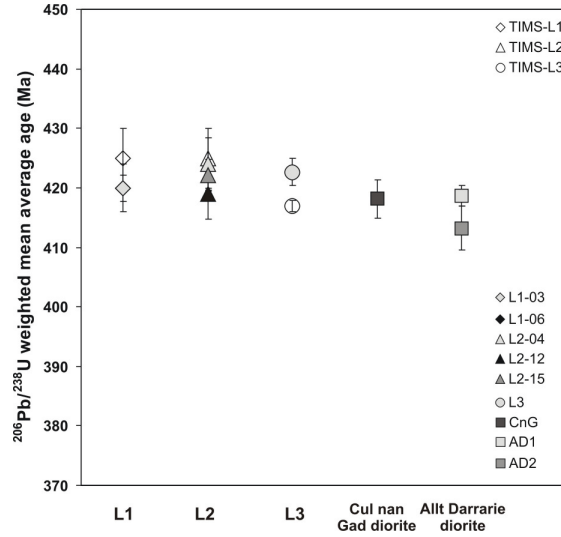
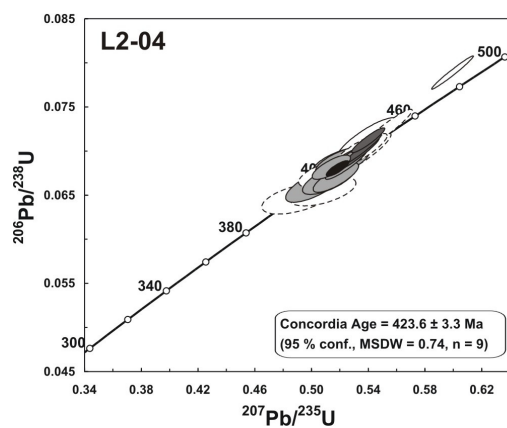
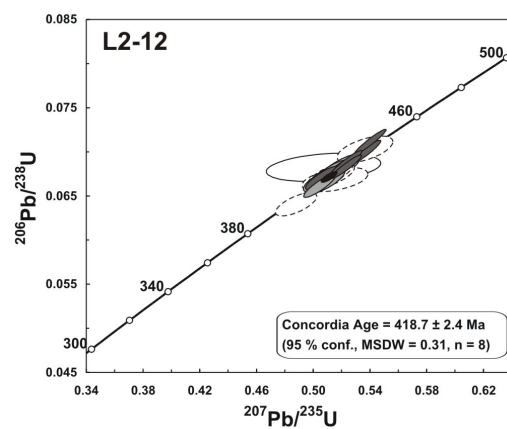
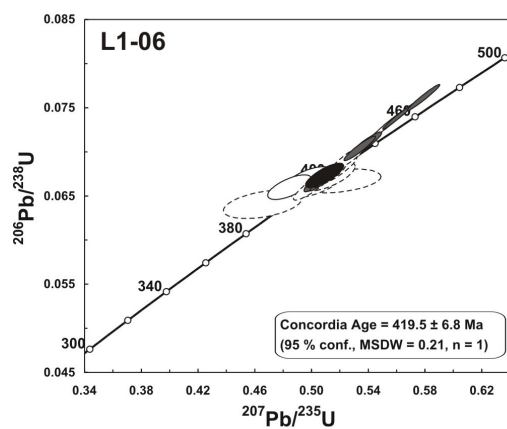
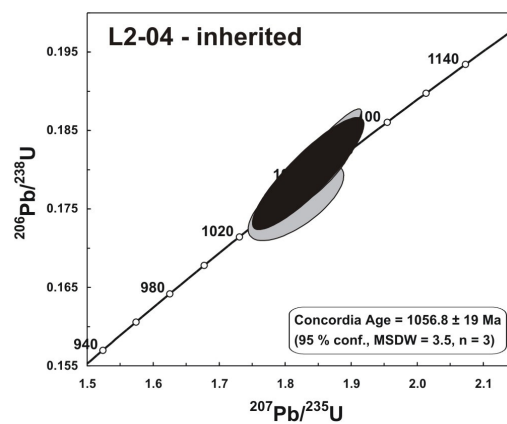
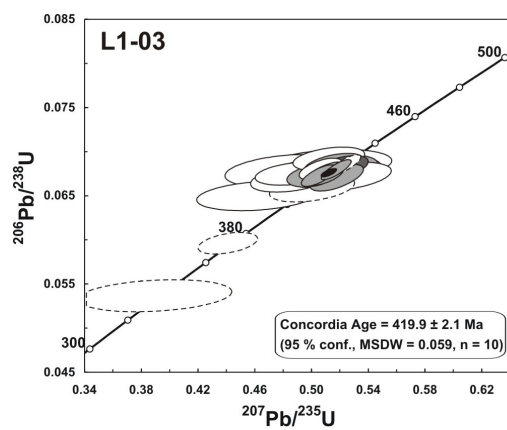


Fig. 4: Weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  ages of the Lochnagar pluton (error bars =  $2\sigma$ ).





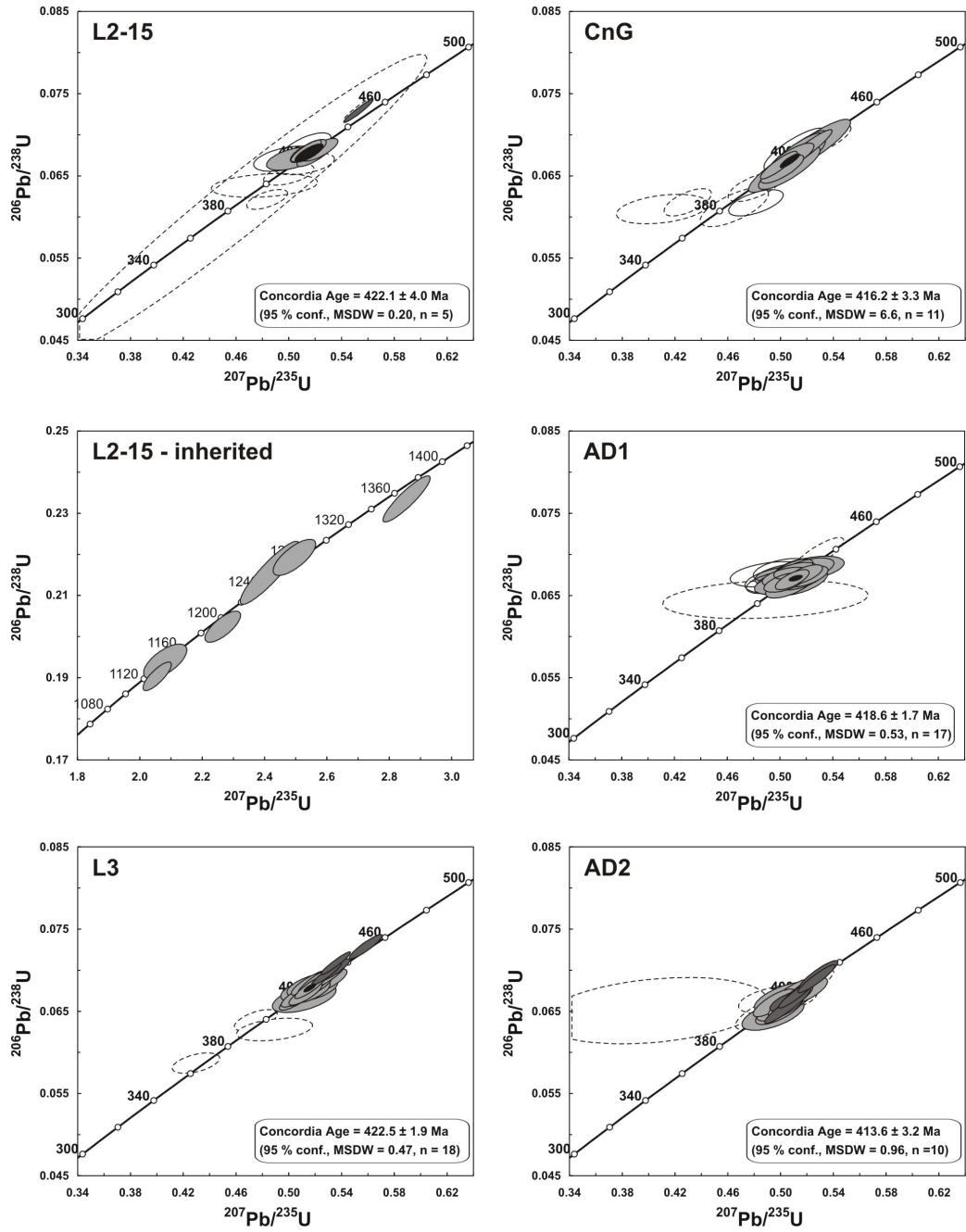


Fig. 5: Concordia diagrams of zircons from the Lochnagar pluton (light grey ellipses = concordant data, dark grey ellipses = data with > 1000 ppm U, white ellipses = > 10 % discordant data, white dashed ellipses = data from cracks, inclusions and with high common Pb; error ellipses =  $2\sigma$ ).

Table 2  
Averaged zircon data from the Lochnagar pluton

Sample	L1-03	L1-06	L2-04	L2-12	L2-15	L3
Age [Ma]	420	420	424	419	422	423
1 $\sigma$	2	n=10 4	5	n=9 4	n=8 3	n=5 2
n=18						
Trace elements [ppm]						
Th	140	1224	333	883	252	538
U	243	2932	1456	1475	698	885
P	319	869	552	640	514	586
Ti	10	6	6	8	52	8
Y	769	3436	1584	2471	1229	1756
HfO <sub>2</sub> [wt%]	1.3	1.5	1.7	1.3	1.4	1.3
REEs [ppm]						
La	0.6	2.6	0.7	2.6	1.1	1.5
Ce	31.0	196.3	44.2	109.0	46.3	73.0
Pr	0.6	3.6	0.4	2.2	1.1	1.1
Nd	5.4	24.6	3.9	16.0	9.8	9.0
Sm	4.5	20.3	6.0	15.8	7.3	9.8
Eu	1.3	1.9	1.2	3.1	1.8	2.2
Gd	20	89	35	75	29	48
Tb	7	32	13	25	10	16
Dy	81	395	166	287	120	195
Ho	30	139	62	99	45	71
Er	146	651	299	450	217	334
Tm	32	133	64	91	48	69
Yb	260	997	516	684	402	544
Lu	61	220	116	154	101	123
Yb <sub>N</sub> /La <sub>N</sub>	606	556	1089	373	519	510
Yb <sub>N</sub> /Gd <sub>N</sub>	18	15	20	12	18	14
Eu/Eu*	0.48	0.19	0.26	0.27	0.33	0.32
Ce/Ce*	67.3	44.4	71.1	55.1	84.3	53.4
Oxygen isotopes						
$\delta^{18}\text{O}$ [‰]	6.4	6.3	7.3	6.4	6.6	6.7
2 $\sigma$	0.6	0.5	7.3	6.4	0.7	0.5

Sample		CnG		inherited zircons						
Age [Ma]		AD1	AD2	inh L2-04	inh L2-15 (1)	inh L2-15 (2)	inh L2-15 (3)			
1 $\sigma$	418 3	n=11 419 2	n=17 413 4	n=10 1046 33	n=3 1149 18	n=2 1235 45	n=3 85 (37-89) 187 (92-242) 262 (72-332) 8 (12-15) 1745 (767-1626) 1 (1.0-1.5)	n=2 102 278 296 4 1766 1.6	n=1 1397 9	
Trace elements [										
Th	293 (40-928)	n=14 168	n=18 1309	(49-5255) n=7 94	(35-173) n=3 64	(83-86) n=3 153	(149-225) n=2 187	(92-242) n=1 278		
U	345 (80-641)	153 (45-461)	1044 (297-2935)	207 (59-398)	153 (149-225)	262 (72-332)	8 (12-15)	4		
P	205 (61-533)	291 (172-534)	211 (35-599)	332 (270-365)	245 (244-279)	13 (8-9)	17 (11-25)	13 (8-9)		
Ti	8 (4-14)	14 (7-26)	5 (2-12)	743 (634-862)	1156 (1229-2260)	1.3 (1.1-1.5)	1.5 (1.3-1.7)	1.3 (1.1-1.5)		
Y	734 (162-2102)	1160 (420-4174)	1600 (129-5311)	1.5	1.3	1.3	1.3	1.3		
HfO <sub>2</sub> [wt%]	1.1 (0.9-1.7)	1.2 (0.9-1.6)	1.3 (1.0-1.5)							
REEs [ppm]										
La	0.4 (0.0-3.5)	0.1 (0.0-0.7)	0.4 (0.0-2.1)	0.0 (0.05-0.31)	0.0 (0.15-0.23)	0.0 (0.10-0.26)	0.0	0.0		
Ce	14.8 (6.1-20.7)	20.3 (7.0-73.0)	53.2 (3.7-177.6)	33.4 (35.6-77.7)	16.9 (25.23-38.67)	19.3 (19.98-41.18)	7.3	7.3		
Pr	0.3 (0.0-0.6)	0.3 (0.1-1.1)	0.9 (0.0-2.9)	0.1 (0.8-1.3)	0.2 (1.50-7.18)	0.4 (0.83-4.44)	0.2	0.2		
Nd	3.3 (0.3-6.8)	4.4 (1.0-15.9)	10.4 (0.2-40.7)	1.8 (2.5-5.4)	3.8 (4.29-20.87)	5.7 (3.01-18.24)	3.8	3.8		
Sm	3.6 (0.6-12.2)	5.7 (1.8-19.4)	10.9 (0.2-47.8)	3.0 (14-27)	6.2 (30-99)	9.5 (19-82)	6.7	6.7		
Eu	1.9 (0.2-7.0)	2.3 (0.7-7.4)	4.8 (0.1-21.2)	0.5 (7-11)	1.0 (3-10)	0.4 (4-43)	0.8	0.8		
Gd	18 (3-67)	30 (9-110)	48 (1-194)	16 (60-99)	31 (138-325)	45 (74-275)	44	44		
Tb	6 (1-20)	10 (3-37)	15 (1-59)	6 (125-185)	12 (288-606)	16 (156-518)	16	16		
Dy	70 (13-227)	121 (39-460)	180 (8-662)	75 (242-365)	134 (541-1040)	192 (316-878)	189	189		
Ho	26 (5-79)	46 (15-169)	63 (4-218)	28 (409-604)	47 (890-1594)	69 (513-1276)	71	71		
Er	137 (27-385)	230 (80-833)	307 (27-997)	146 (739-1120)	213 (1486-2493)	316 (874-1912)	337	337		
Tm	33 (7-86)	51 (19-181)	67 (8-206)	32 (1118-1629)	42 (2037-3101)	62 (1228-2362)	70	70		
Yb	296 (70-762)	427 (165-1465)	553 (83-1647)	269 (1406-2056)	314 (2381-3333)	464 (1475-2378)	577	577		
Lu	77 (20-177)	103 (42-339)	129 (27-352)	63 (2271-3126)	66 (3573-5150)	106 (2313-3082)	135	135		
Yb <sub>N</sub> /La <sub>N</sub>	1076 (45-18225)	5655 (776-22406)	1918 (436-12758)	8552 (6594-29113)	11234 (14376-15566)	14971 (9239-15206)	25314	25314		
Yb <sub>N</sub> /Gd <sub>N</sub>	30 (18-40)	20 (11-30)	32 (10-79)	20 (15.1-23.3)	15 (10.3-17.3)	14 (8.7-19.9)	15.8	15.8		
Eu/Eu*	0.68 (0.46-0.90)	0.56 (0.47-0.65)	0.58 (0.48-0.69)	0.20 (0.16-0.23)	0.16 (0.0-0.1)	0.05 (0.1-0.3)	0.14	0.14		
Ce/Ce*	30.0 (3.4-84.3)	41.8 (8.8-143.5)	40.6 (8.0-109.2)	153.9 (68.3-269.5)	48.2 (30.0-52.6)	41.3 (35.8-70.3)	21.4	21.4		
Oxygen isotopes										
$\delta^{18}\text{O}$ [‰]	6.0 (5.5-6.4)	n=36 7.1 (6.1-8.1)	n=41 6.6 (5.9-7.5)	n=32 6.2 (5.9-7.5)	n=3 5.9	n=2 5.9	n=5 5.9	n=3 6.8	n=3 6.8	
2 $\sigma$	0.5	0.4	0.5	0.5	0.5	0.5	0.5	0.9	0.9	

#### 4.4. Zircon REE/trace element data

Lochnagar zircons display REE patterns typical of zircons from granitoid rocks, with strong HREE-enrichment ( $\text{Yb}_\text{N}/\text{La}_\text{N}=45\text{-}22406$ ), a positive Ce anomaly ( $\text{Ce}/\text{Ce}^*$ ) and a negative Eu anomaly ( $\text{Eu}/\text{Eu}^*$ ) (Fig. 6). Minor variation in the overall REE abundances and in the degree of  $\text{Eu}/\text{Eu}^*$  occurs between and within samples and even within single grains; however no systematic change was recognised. On average, zircons from diorite CnG contain the lowest REE abundances (except La and Eu), whereas those of granite L1-06 contain the highest. The diorite zircons have the weakest Eu anomalies ( $\text{Eu}/\text{Eu}^* = 0.56\text{-}0.68$  (AD1 and CnG, respectively) and L1-06 zircons the strongest ( $\text{Eu}/\text{Eu}^* = 0.19$ ). This suggests the melt experienced more calcic-feldspar fractionation prior to zircon crystallisation in the granites than in the diorites.

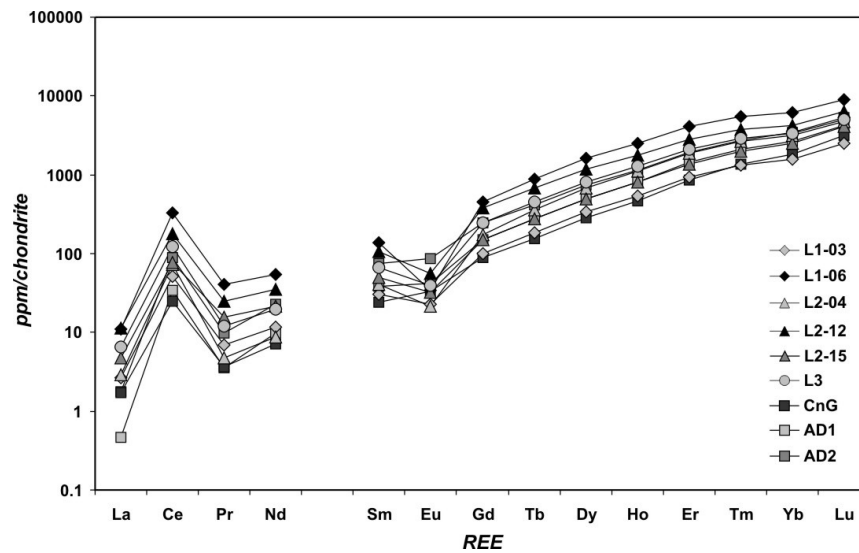


Fig. 6: Average zircon REE patterns of the Lochnagar pluton normalised to chondrite using values of Anders and Grevesse (1989).

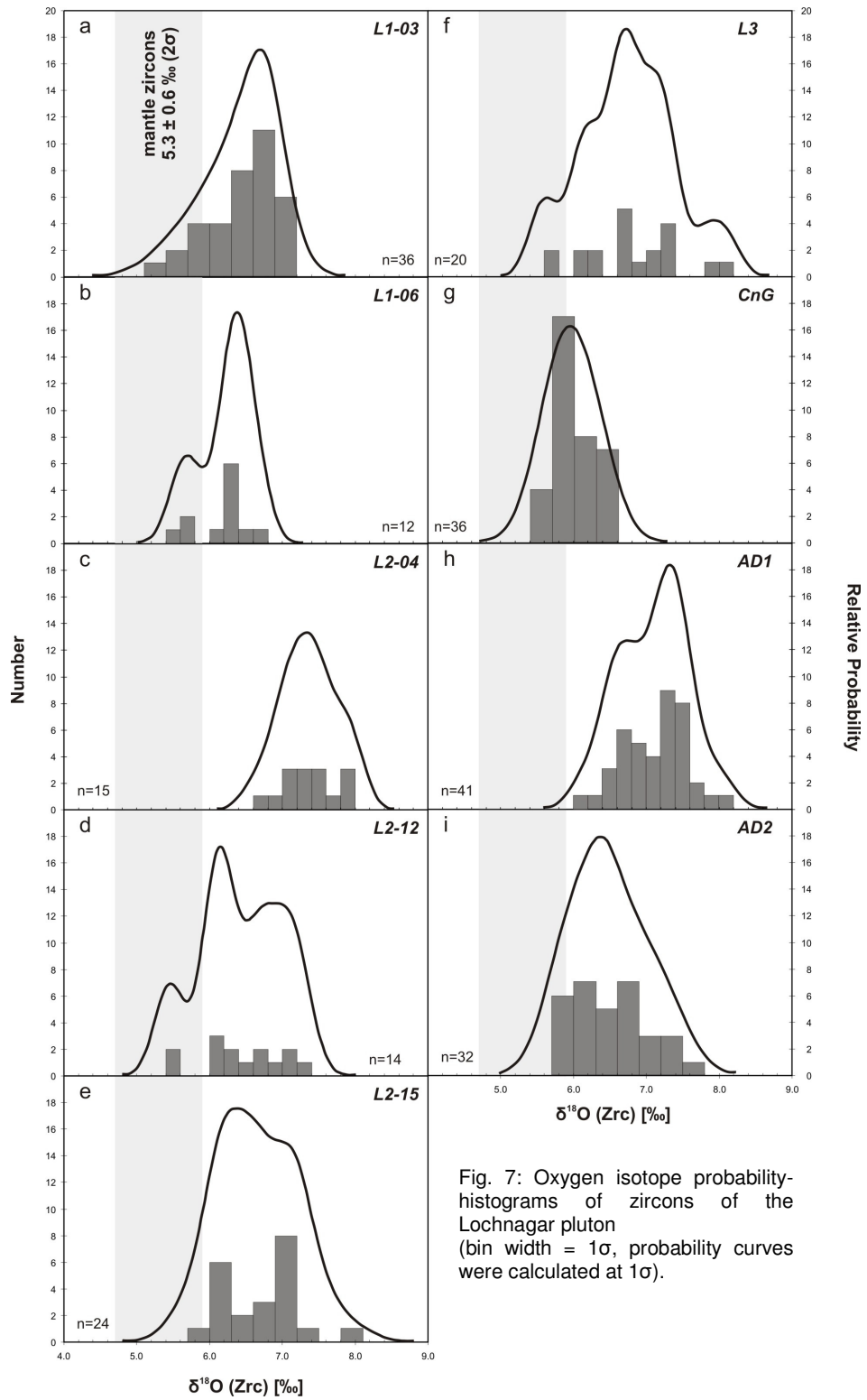


Fig. 7: Oxygen isotope probability-histograms of zircons of the Lochnagar pluton (bin width =  $1\sigma$ , probability curves were calculated at  $1\sigma$ ).

#### 4.5. Zircon oxygen isotope data

Lochnagar zircons range in  $\delta^{18}\text{O}$  from 5.3 to  $8.1 \pm 0.6 \text{‰}$  ( $n=230$ ,  $2\sigma$ ) (Fig. 7a-i) with a mean of  $6.6 \pm 0.6 \text{‰}$  ( $2\sigma$ ). For comparison, mantle zircons have  $\delta^{18}\text{O}$  values of  $5.3 \pm 0.6 \text{‰}$  ( $2\sigma$ , Valley et al. 1998). On a sample scale each sample displays a different mean  $\delta^{18}\text{O}$  value; the lowest value occurs in zircons of the CnG diorite ( $6.0 \pm 0.4 \text{‰}$  ( $2\sigma$ )) and the highest in those of granite sample L2-04 ( $7.3 \pm 0.5 \text{‰}$  ( $2\sigma$ )). However, the main differences between samples, both within a single Lochnagar facies and between different facies, lie in the range and distribution of oxygen isotope values. Zircons in diorite CnG form the tightest data group with a clear unimodal distribution and a spread of  $0.9 \text{‰}$  ( $5.5\text{--}6.4 \text{‰}$ ), which is similar to the degree of heterogeneity observed in standard 91500 analysed in the same analytical session. All other samples are more heterogeneous and show  $\delta^{18}\text{O}$  ranges from  $1.1 \text{‰}$  (L1-06) to  $2.5 \text{‰}$  (L3). Distribution patterns vary between almost unimodal (diorite AD2, L1-03, L2-04), bimodal (diorite AD1, L1-06, L2-15) and random with no distinct modes (L2-12, L3). Detailed examination of the inter- and intra-grain scale variation of the samples shows that the spread in  $\delta^{18}\text{O}$  results predominantly from variation between zircon crystals. However, in zircons of diorites AD2 and CnG, and in granite L3 resolvable variation was also found within crystals (between cores and rims, within core domains c1 and c2, and within the same zone). In these samples both an increase and a decrease in  $\delta^{18}\text{O}$  with zircon growth was observed.

Inherited grains were also analysed for their oxygen isotope composition. The single inherited zircon discovered in L2-04 displays a mean  $\delta^{18}\text{O}$  value of  $6.2 \pm 0.5 \text{‰}$  ( $n=3$ ); five inherited grains of sample L2-15 show a much larger range ( $5.2\text{--}7.5 \text{‰}$ ), but the same mean of  $6.2 \pm 0.5 \text{‰}$  ( $n=9$ ).

### 5. The Etive pluton

The Etive pluton, which is representative of the Argyll suite, intruded into Dalradian metasediments and is exposed over an elliptical area of approximately  $300 \text{ km}^2$  (Fig. 8). It can be described as a major composite pluton, which comprises four

main intrusive phases ranging in composition from granite to monzodiorite/diorite (Stephenson et al., 1999).

The medium- to coarse-grained *Quarry Intrusion* represents the outermost intrusion of the pluton and is exposed as a small lens of diorite/quartz-diorite. It commonly contains metasedimentary country rock xenoliths and microdioritic or appinitic enclaves (Clayburn et al., 1983; Stephenson et al., 1999).

The largest part of the pluton comprises the compositionally heterogeneous *Cruachan Intrusion*, which ranges from granite through tonalite/granodiorite to monzodiorite and contains abundant microgranitoid enclaves (Jacques and Reavy, 1994). Two main rock types have been distinguished – pale grey, medium-grained, equigranular monzogranites with occasional mafic clots and metasedimentary xenoliths, which predominantly occur in the northern lobe of the intrusion, and grey, medium- to fine-grained monzodiorites, which are abundant in the southern lobe (Batchelor, 1987).

The *Meall Odhar Intrusion* has been described as a pink K-feldspar and quartz granite sheet and dyke intrusion, which cross-cuts all the earlier phases. However, field work carried out for this study has identified numerous locations where the Cruachan Intrusion intrudes the Meall Odhar Intrusion. Similar to the other facies, it is compositionally variable and comprises fine- to medium-grained syenogranites and monzogranites (Stephenson et al., 1999).

The centre of the Etive pluton is composed of the elliptical *Starav Intrusion*. It comprises at least two separate magma pulses, which are represented by two concentric intrusions – the porphyritic, medium- to coarse-grained Outer Starav Facies and the medium-grained non-porphyritic Inner Starav Facies (Batchelor, 1987; Clayburn et al., 1983; Jacques and Reavy, 1994).

To summarise, based on field relationships the pluton becomes younger towards the centre with the order of emplacement being Quarry Intrusion, approximately contemporaneously Cruachan and Meall Odhar intrusions, and Starav Intrusion (Bailey, 1960) (for a more detailed description of the facies' petrography and field relationships see Table 3).

Early radiometric data for the pluton obtained by Rb-Sr, Ar-Ar, K-Ar and U-Pb zircon TIMS dating methods yielded ages ranging from 410 Ma to 373 Ma (Brown,

1975; Brown et al., 1968; Clayburn, 1981; Clayburn et al. 1983; Halliday et al., 1979; Harmon and Halliday, 1980; Pankhurst, 1982; Pidgeon and Aftalion, 1978). Based on these dates and their interpretation, Clayburn et al. (1983) concluded that the Etive Complex was emplaced approximately contemporaneously at 400 Ma. However, more recently Morris et al. (2005) obtained Ar-Ar biotite ages of  $415 \pm 1.8$  Ma and  $414 \pm 2$  Ma for the Etive dyke swarm, which they interpreted to mark the end of magmatism.

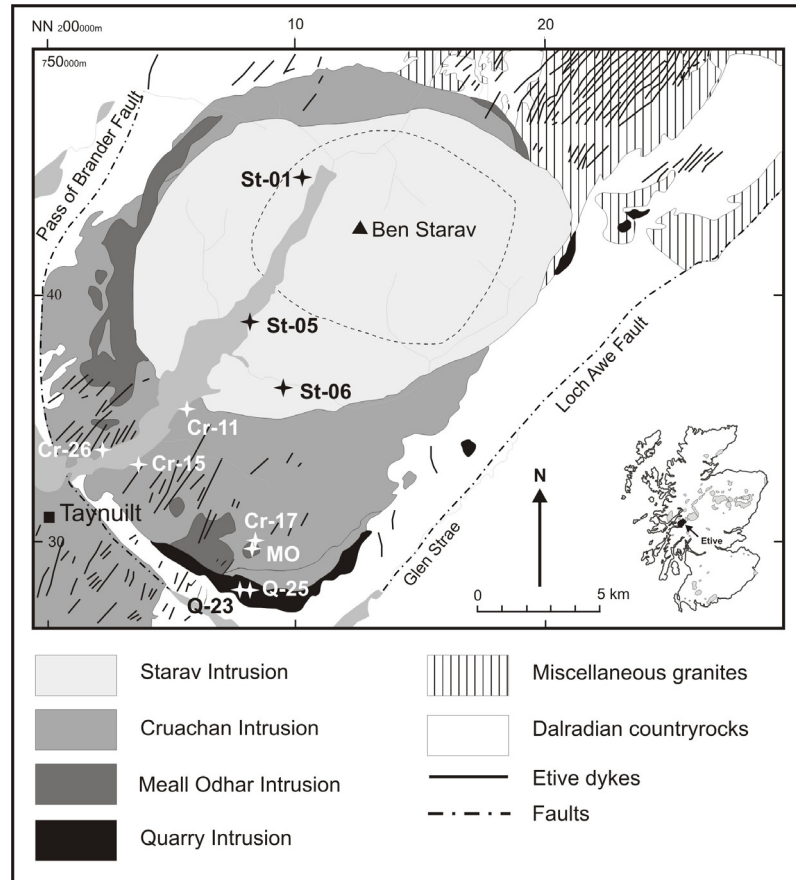


Fig. 8: Geological sketch map of the Etive pluton with sample locations (after Anderson, 1937; Batchelor, 1987).

The Etive pluton has been studied more extensively than the Lochnagar pluton in terms of its Nd and Sr isotope composition, and data exist for all intrusive phases. All have negative  $\epsilon\text{Nd}_{400 \text{ Ma}}$  values ranging from -4.7 to -9.3, with the Cruachan Intrusion displaying the least negative  $\epsilon\text{Nd}$  and the Starav Intrusion and one sample of the Quarry Intrusion showing the most negative  $\epsilon\text{Nd}$  values (Frost and O’Nions, 1985).



Initial  $^{87}\text{Sr}/^{86}\text{Sr}$  values range from 0.7043 to 0.7068. Based on the Nd isotope data, the Etive pluton contains a larger crustal component than the Lochnagar pluton, although Sr isotope data do not support this. The petrogenetic model of Clayburn et al. (1983) interpreted the Etive pluton to be the result of melting of a lower crustal and a mantle component. The different phases are assumed to be derived from the same source, with the later phases such as the Starav Intrusion containing a larger crustal component (Clayburn et al., 1983). However, a later detailed whole-rock geochemical study (Batchelor, 1987) has suggested that the Etive pluton has a much more complicated petrogenetic history; it was not entirely derived from the same source and was emplaced as numerous separate magma pulses. At present, the nature of the crustal component and the individual mantle and crustal proportions that have been involved in the generation of the Etive pluton are still unresolved.

### *5.1. Samples*

Ten samples representative of the four main Etive pluton facies, the Quarry Intrusion (Q-23 & Q-25), Cruachan Intrusion (Cr-11, Cr-15, Cr-17 & Cr-26), Meall Odhar Intrusion (MO) and Starav Intrusion (St-01, St-05 & St-06), were selected for analyses. All samples, except those of the Starav Intrusion, differ to some degree from the published petrographic data (see Table 3). The Quarry Intrusion samples contain higher abundances of plagioclase (55-60 %) and biotite (20 %), but less quartz (5 %) than previously reported, while pyroxene was not observed. Of the Cruachan Intrusion samples (all were collected in the southern lobe) only Cr-26 is consistent with the published data. Cr-11 and Cr-17 contain 10-20 % hornblende, which has not been reported in the literature, and only Cr-17 comprises K-feldspar. The Meall Odhar Granite sample is strongly biotite- and plagioclase-phyric (up to 3 mm) and compositionally resembles the monzogranitic variant described in the literature.

**Table 3**  
**Summary of published petrographic and field relationship data of the Eive pluton**

	<b>lithology</b>	<b>colour</b>	<b>grain size</b>	<b>texture</b>	<b>major phases</b>	<b>accessory phases</b>	<b>field relationships</b>
<b><u>Eive</u> Quarry Intrusion</b>	qtz diorite		medium- to coarse-grained	plag-phyrlic (up to 15 mm)	plag (46%), hbl (20%), qtz (12%), bt titanite, apatite, (12%), pyx (9%)	zircon, opaques	transitional contact between variants, contains country rock xenoliths
	diorite		medium-grained	pyx-phyrlic (up to 8 mm), mafic clusters of amph + bt after pyx			
<b>Cruachan Intrusion</b>	monzogranite (northern lobe)	pale grey	medium-grained (2-5 mm)	equigranular with mafic clusters	plag (30-46%), Kspar (23-34%), qtz titanite, apatite, (16-28%), bt (4.5-6.5%), hbl (3-9.5%)	zircon, opaques	intrudes Meall Odhar I., contains country rock xenoliths
	monzodiorite (southern lobe)	grey to dark-grey	medium- to fine-grained (1-5 mm)	equigranular	subhedral plag (54-63%); interstitial titanite, Fe-Ti Kspar (7-25%), bt (6-21%), qtz (5-12%)		
	syenogranite	pink	fine- to medium-grained (< 3 mm)		Kspar (50-67%), qtz (27-37%), plag chlorite, zircon, (4.5-12%), hbl (0.2-2%)	opaques, titanite, apatite	intrudes Cruachan I. as sheets and dykes, but also cut by Cruachan I.; cut by Starav I.
<b>Meall Odhar Intrusion</b>	monzogranite	pink	fine- to medium-grained (< 3 mm)		qtz (30-42%), Kspar (33-41%), plag titanite, opaques, (20-28%), bt (0.5-1%)	apatite, zircon	
	monzogranite (Outer Facies)	pink-grey	medium- to coarse-grained (1-10 mm)	Kspar (up to 30 mm) + hbl (0.5-2 mm) phyrlic; mafic clusters of hbl, bt, opaques	Kspar (27-46%), plag (23-41%), qtz titanite, apatite, (21-32%), bt (3-6%), hbl (0.2-6%)	zircon, opaques	
	monzogranite (Inner Facies)		medium-grained (2-5 mm)	equigranular	Kspar (27-48%), qtz (28-40%), plag titanite, apatite, (22-36%), bt (1-3%)	zircon, opaques, monazite, thorite	

data from Batchelor (1987) and Stephenson et al. (2000)

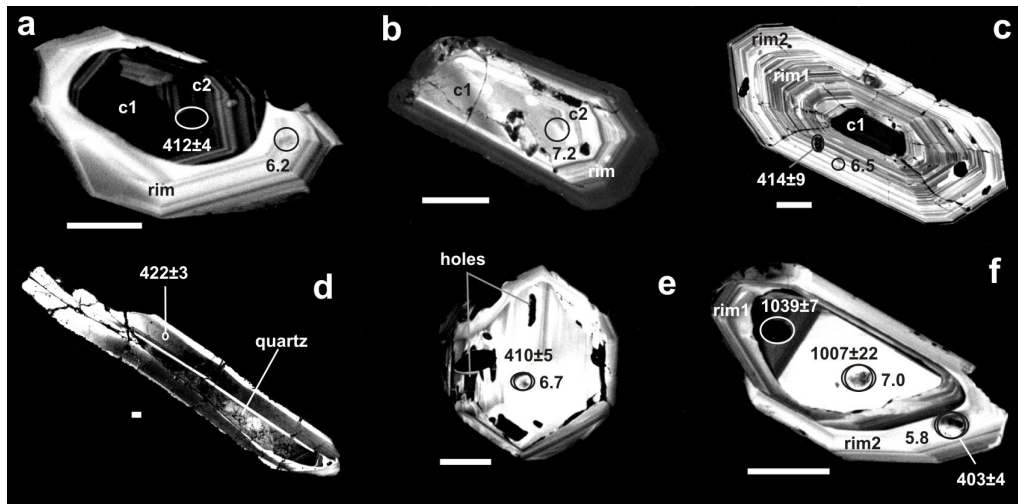


Fig. 9: CL images of representative zircons from the Etive pluton with correlating  $\delta^{18}\text{O}$  values and U-Pb ages.

a) Zircon comprising weakly luminescent core (unzoned inner domain (c1) + zoned outer domain (c2)) and single strongly luminescent zoned rim. CL intensity varies only little between zones (grain 17, Cr-26)

b) Zircon with strongly luminescent core (c1 + c2) and single zoned rim found in samples of the Starav Intrusion. Rim comprises two main zones, which vary strongly in CL intensity (grain 7, St-01).

c) Crystal showing small weakly luminescent resorbed core and two large zoned rims. Zones within rims are very narrow and vary strongly in CL intensity (grain 19, St-01).

d) Acicular very large zircon crystal with quartz in the centre; crystals were observed in Cr-11 of the Cruachan Intrusion, and Q-23 and Q-25 of the Quarry Intrusion (grain 21, Cr-11).

e) Equant zircon crystal with holes found in Cr-11 of the Cruachan Intrusion, and Q-23 and Q-25 of the Quarry Intrusion (grain 22, Q-23).

f) Xenocrystic core with two magmatic rims (grain 4, Cr-15).

(Scale bar = 50  $\mu\text{m}$ ; circles indicate oxygen isotope analyses; ovals U-Pb analyses; quoted U-Pb error = 1 $\sigma$ ,  $\delta^{18}\text{O}$  error = 0.3-0.5 (2 $\sigma$ )).

## 5.2. Zircon morphologies

Zircon crystals from the Etive pluton share the majority of features described for zircons of the Lochnagar pluton, including a range of sizes (75  $\mu\text{m}$  to > 2 mm, mostly 200-250  $\mu\text{m}$ ), morphologies (equant to acicular, mostly stubby) and internal zoning patterns (sector zoning was only observed in zircons from the Meall Odhar Intrusion sample). In the Meall Odhar, Cruachan and Starav intrusions all zircon crystals also comprise obvious cores and rims, which are separated by resorption surfaces. Commonly cores are weakly to moderately luminescent in CL (Fig. 9a), but in the Starav samples approximately half the crystals consist of a strongly luminescent core (Fig. 9b). Cores are either unzoned (c1) or zoned (c2) and commonly represent the largest part in a crystal. In the latter case crystals usually comprise an inner unzoned (c1) domain and an outer zoned (c2) domain (Fig. 9a &

b). Zircon rims commonly consist of zones, which may vary in width and CL intensity between crystals (Fig. 9a & c).

Zircons from Cruachan Intrusion sample Cr-11 and those of the Quarry Intrusion have very different morphology and internal zoning to those of the other Etive samples. All three samples comprise two zircon populations, with the more prominent one consisting of elongated to acicular grains that may be larger than 2 mm (Fig. 9d). The second population displays smaller (up to 250  $\mu\text{m}$ ) equant to stubby crystals (Fig. 9e). In both populations grain centres commonly contain quartz or holes, which are surrounded by moderately to strongly luminescent broad zones. It is not clear whether the central quartz represents restitic material on which the zircons nucleated, which may explain the large grain size, or if the zircons contained holes and were subsequently infilled by quartz.

Inherited grains occurring in Cruachan Intrusion samples Cr-15 and Cr-17 were only detected by U-Pb age dating, as the zoning patterns are not strikingly different (Fig. 9f).

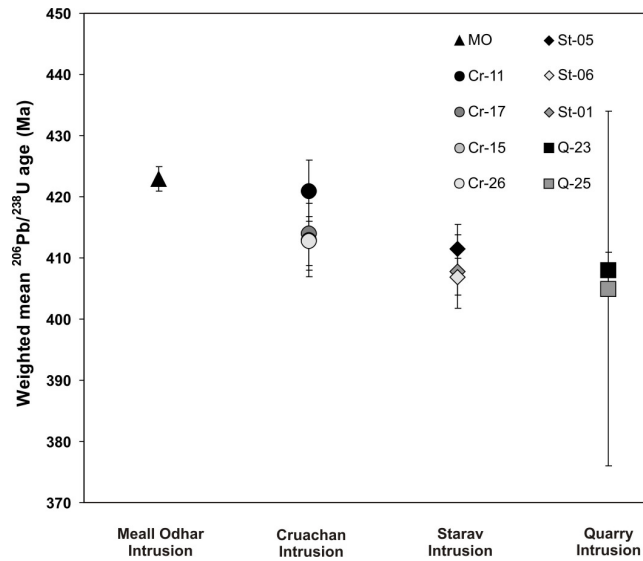
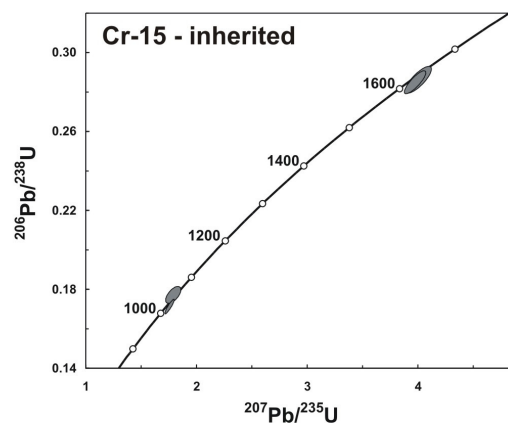
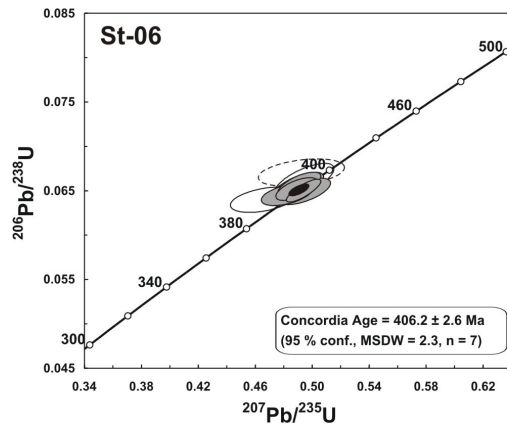
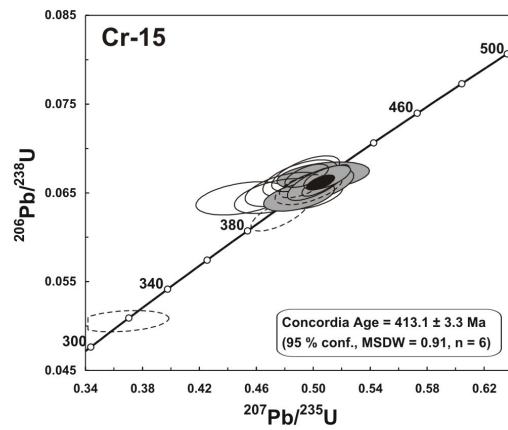
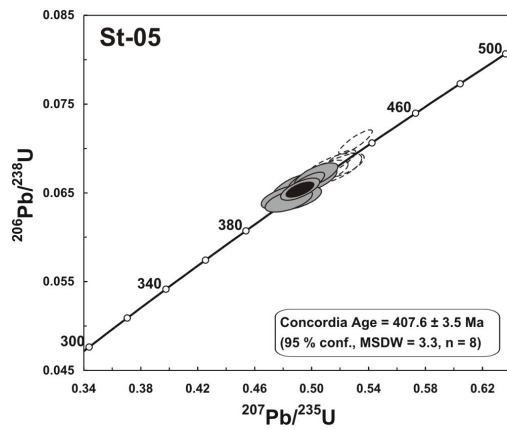
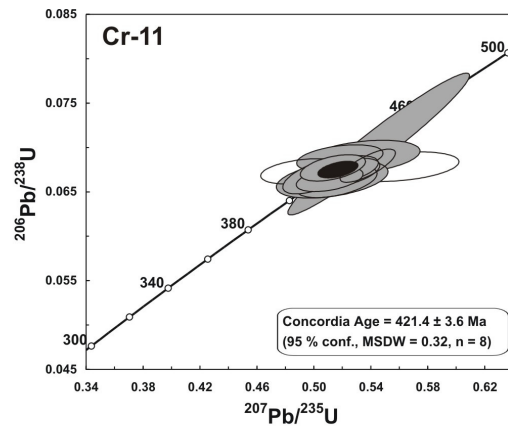
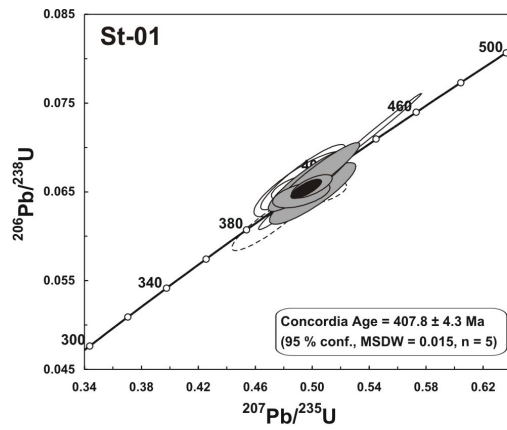


Fig. 10: Weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  ages of the Etive pluton (error bars =  $2\sigma$ ).



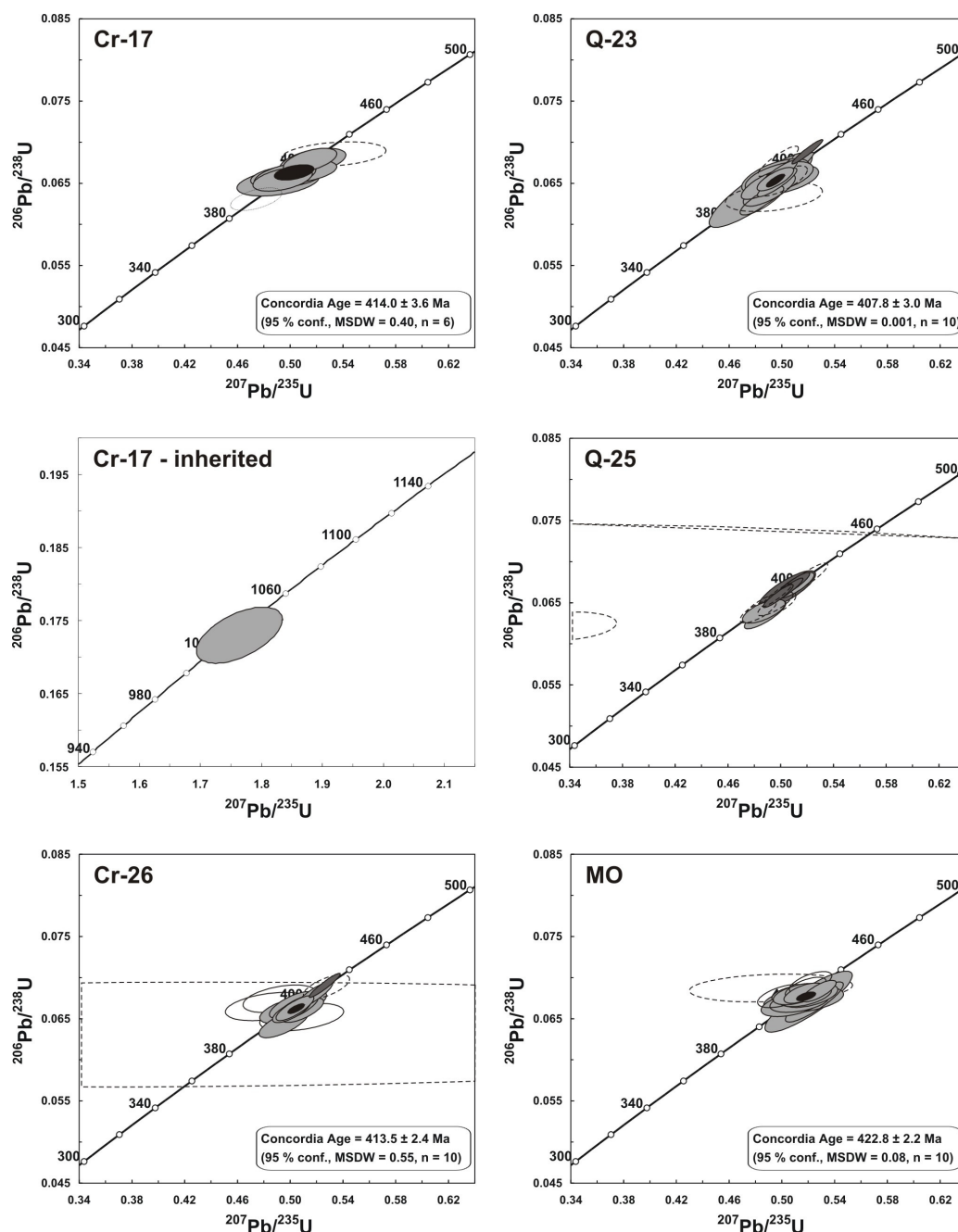


Fig. 11: Concordia diagrams of zircons from the Etive pluton (light grey ellipses = concordant data, dark grey ellipses = data with > 1000 ppm U, white ellipses = > 10 % discordant data, white dashed ellipses = data from cracks, inclusions and with high common Pb; error ellipses =  $2\sigma$ ).

### 5.3. U-Pb data

The oldest samples from the Etive pluton are the Meall Odhar Intrusion, with an age of  $423 \pm 2$  Ma, and Cr-11 of the Cruachan Intrusion at  $421 \pm 5$  Ma. The remaining Cruachan samples yield younger ages of  $414 \pm 6$  Ma (Cr-17),  $413 \pm 6$  Ma (Cr-15) and  $413 \pm 4$  Ma (Cr-26). St-05 of the Starav Intrusion intruded at  $412 \pm 6$  Ma (contemporaneously with the Cruachan samples), and the remaining Starav intrusion samples St-01 and St-06 somewhat later at  $408 \pm 4$  Ma and  $407 \pm 3$  Ma, while the Quarry Intrusion is dated at  $408 \pm 3$  Ma (Q-23) and  $405 \pm 29$  (Q-25). Thus, the Etive pluton was emplaced over a period of approximately 16 m.y. (Fig. 10 & 11).

Inherited zircon crystals were observed only in Cr-15 and Cr-17 of the Cruachan Intrusion. Cr-15 contains two inherited grains (out of 14 analysed grains) with  $^{207}\text{Pb}/^{206}\text{Pb}$  ages of  $1036 \pm 110$  Ma and  $1646 \pm 10$  Ma. In Cr-17 only one older grain (out of 12 analysed grains) was found, which gives a  $^{207}\text{Pb}/^{206}\text{Pb}$  age of  $1040 \pm 25$  Ma.

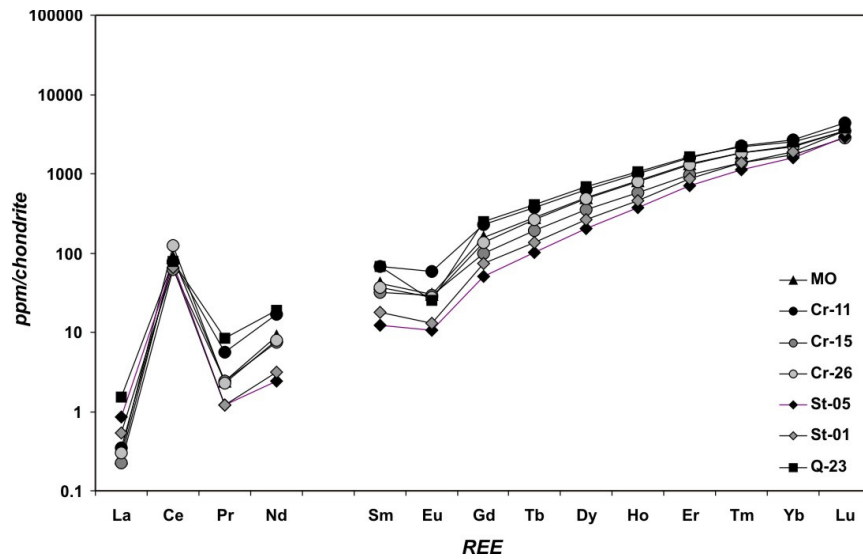


Fig. 12: Average zircon REE patterns of the Etive pluton normalised to chondrite using values of Anders and Grevesse (1989).

Table 4

Averaged zircon data from the Etive pluton

Sample	MO	Cr-11	Cr-17	Cr-15	Cr-26	
Age [Ma]	423 ± 2	421 ± 5	n=8 414 ± 6	n=7 413 ± 6	n=6 413 ± 4	n=10
Trace elements [ppm]						
Th	136 (53-325)	235	n=11 89	(49-219) n=7 100	(44-286) n=9 453	(30-2680) n=8
U	174 (82-315)	234	(184-412)	(74-206) 134	(60-473) 490	(48-2933)
P	364 (285-534)	280	(170-480)	271	(161-392) 329	(131-812)
Ti	21 (10-107)	9	(5-12)	12	(4.8-26.5) 11	(7-16)
Y	1152 (742-1871)	1404	(783-2839)	820	(400-1234) 1117	(266-3909)
HfO <sub>2</sub> [wt%]	1.0 (1.0-1.1)	1.0	(0.9-1.2)	1.0	(0.9-1.4)	1.1 (0.9-1.4)
REEs [ppm]						
La	0 (0.0-0.1)	0	(0.0-0.2)	0	(0.0-0.1)	0 (0.0-0.2)
Ce	53 (23.5-101.1)	48	(35.2-85.0)	38	(19.2-80.2)	75 (25.2-282)
Pr	0 (0.1-0.3)	0	(0.1-1.2)	0	(0.1-0.5)	0 (0.0-0.5)
Nd	4 (1.7-6.4)	8	(2.2-17.1)	3	(1.2-8.2)	4 (0.5-8.1)
Sm	6 (3.7-9.2)	10	(3.4-23.7)	5	(1.8-8.5)	5 (1.1-13)
Eu	2 (1.1-2.5)	3	(1.0-8.1)	2	(0.8-3.3)	2 (0.4-3.2)
Gd	31 (19-43)	45	(17-110)	19	(10-38)	27 (6-79)
Tb	10 (6-15)	14	(6-32)	7	(3-12)	10 (2-32)
Dy	121 (78-186)	153	(71-337)	86	(42-140)	117 (25-412)
Ho	45 (28-73)	55	(29-115)	32	(16-48)	44 (11-155)
Er	212 (134-351)	256	(150-504)	154	(76-237)	207 (50-740)
Tm	45 (29-74)	54	(34-103)	34	(16-55)	44 (12-156)
Yb	356 (226-594)	440	(297-812)	280	(141-495)	365 (100-1262)
Lu	83 (54-138)	106	(77-186)	69	(35-121)	85 (25-277)
Yb <sub>N</sub> /La <sub>N</sub>	8318 (4025-11637)	7835	(5289-11210)	7706	(3737-13806)	7516 (2403-16849)
Yb <sub>N</sub> /Gd <sub>N</sub>	14 (11-17)	14	(9-22)	19	(11-43)	17 (10-22)
Eu/Eu*	0.37 (0.32-0.42)	0.47	(0.41-0.50)	0.52	(0.42-0.66)	0.45 (0.15-0.54)
Ce/Ce*	118 (51.6-184.2)	74	(34.7-135.6)	110	(20.9-249.3)	167 (31.0-345.6)
Oxygen isotopes						
δ <sup>18</sup> O [‰]	6.5 ± 0.5 (5.5-8.2)	n=30	6.9 ± 0.4 (5.7-7.9)	n=26 4.7 ± 0.4 (4.6-7.5)	n=32 6.2 ± 0.4 (5.3-6.9)	n=16 6.4 ± 0.3 (5.3-7.6)



Table 4

Averaged zircon data from the Etive pluton

Sample		MO	Cr-11		Cr-17		Cr-15		Cr-26		St-05		St-06		
Age [Ma]		423	421	n=10	n=8	414	n=7	413	n=6	413	n=10	412	n=11	407	n=7
1σ		2	5		6			6		4		6		3	
Trace elements [ppm]															
Th	136	(53-325)	235	(120-564)	n=11	89	(49-219)	n=7	100	(44-286)	n=9	453	(30-2680)	n=8	
U	174	(82-315)	234	(184-412)		110	(74-206)		134	(60-473)		490	(48-2933)		n=8
P	364	(285-534)	280	(170-480)					271	(161-392)		329	(131-812)		188 (150-242)
Ti	21	(10-107)	9	(5-12)					12	(4.8-26.5)		11	(7-16)		
Y	1152	(742-1871)	1404	(783-2839)					820	(400-1234)		1117	(266-3909)		
HfO <sub>2</sub> [wt%]	1.0	(1.0-1.1)	1.0	(0.9-1.2)					1.0	(0.9-1.4)		1.1	(0.9-1.4)		
REEs [ppm]															
La	0	(0.0-0.1)	0	(0.0-0.2)					0	(0.0-0.1)		0	(0.0-1.0)		
Ce	53	(23.5-101.1)	48	(35.2-85.0)					38	(19.2-80.2)		75	(25.2-282)		
Pr	0	(0.1-0.3)	0	(0.1-1.2)					0	(0.1-0.5)		0	(0.0-0.3)		
Nd	4	(1.7-6.4)	8	(2.2-17.1)					3	(1.2-8.2)		4	(0.5-8.1)		
Sm	6	(3.7-9.2)	10	(3.4-23.7)					5	(1.8-8.5)		5	(1.1-13)		
Eu	2	(1.1-2.5)	3	(1.0-8.1)					2	(0.8-3.3)		2	(0.4-3.2)		
Gd	31	(19-43)	45	(17-110)					19	(10-38)		27	(6-79)		
Tb	10	(6-15)	14	(6-32)					7	(3-12)		10	(2-32)		
Dy	121	(78-186)	153	(71-337)					86	(42-140)		117	(25-412)		
Ho	45	(28-73)	55	(29-115)					32	(16-48)		44	(11-155)		
Er	212	(134-351)	256	(150-504)					154	(76-237)		207	(50-740)		
Tm	45	(29-74)	54	(34-103)					34	(16-55)		44	(12-156)		
Yb	356	(226-594)	440	(297-812)					280	(141-495)		365	(100-1262)		
Lu	83	(54-138)	106	(77-186)					69	(35-121)		85	(25-277)		
Yb <sub>N</sub> /La <sub>N</sub>	8318	(4025-11637)	7835	(5289-11210)					7706	(3737-13806)		7516	(2403-16849)		
Yb <sub>N</sub> /Gd <sub>N</sub>	14	(11-17)	14	(9-22)					19	(11-43)		17	(10-22)		
Eu/Eu*	0.37	(0.32-0.42)	0.47	(0.41-0.50)					0.52	(0.42-0.66)		0.45	(0.15-0.54)		
Ce/Ce*	118	(51.6-184.2)	74	(34.7-135.6)					110	(20.9-249.3)		167	(31.0-345.6)		
Oxygen isotopes															
δ <sup>18</sup> O [‰]	6.5	(5.5-8.2)	n=30	6.9	(5.7-7.9)	n=26	4.7	(4.6-7.5)	n=32	6.2	(5.3-6.9)	n=16	6.4	(5.3-7.6)	n=26
2σ	0.5		0.4		0.4		0.4		0.4		0.4		0.3		n=14

Sample St-01		Q-23		Q-25		Inh Cr-15		Inh Cr-15		Inh Cr-17	
Age [Ma]	408	n=5	408	n=10	405	n=3	1036	n=2	1646	n=2	1040
1 $\sigma$	4		3	29			110	10		25	
Trace elements											
Th	175	(69-528)	n=9	378	(46-1261)	n=12	568	(221-1103)	n=3	14	n=1
U	403	(165-1372)		403	(91-889)		396	(216-639)		30	86
P	249	(90-507)		403	(268-769)					470	307
Ti	3	(2-6)		17	(11-28)					35.29	21.89
Y	766	(401-1199)		1490	(514-4027)					827	658
HfO <sub>2</sub> [wt%]	1.2	(1.0-1.4)		1.2	(1.1-1.3)					1.2	1.2
REEs [ppm]											
La	0	(0.0-0.7)		0	(0.0-1.5)					0.0	0.0
Ce	40	(24.1-55.5)		47	(21.7-91.0)					21.6	35.7
Pr	0	(0-0.3)		1	(0.1-2.3)					0.2	0.1
Nd	1	(0.6-2.5)		9	(2.5-20.3)					2.9	1.7
Sm	3	(1.6-4.7)		10	(2.7-23.7)					5.3	3.0
Eu	1	(0.3-1.3)		1	(0.5-3.3)					1.3	0.6
Gd	14	(7-24)		48	(15-134)					24	15
Tb	5	(3-8)		15	(5-42)					8	6
Dy	64	(32-94)		167	(53-466)					94	67
Ho	26	(13-36)		59	(19-160)					33	25
Er	138	(73-212)		263	(86-692)					145	123
Tm	33	(18-56)		53	(19-136)					30	28
Yb	310	(171-548)		412	(152-1012)					238	238
Lu	85	(47-156)		92	(36-217)					53	57
Yb <sub>N</sub> /La <sub>N</sub>	3544	(568-13800)		1654	461-14721					8713	7937
Yb <sub>N</sub> /Gd <sub>N</sub>	28	(16-50)		12	(9-22)					12	19
Eu/Eu*	0.36	(0.23-0.41)		0.22	(0.17-0.28)					0.34	0.26
Ce/Ce*	155	(14.8-257.8)		61	(8.0-190.5)					64.9	135.0
Oxygen isotopes											
$\delta^{18}\text{O}$ [‰]	6.9	(6.3-7.4)	n=17	6.3	(5.5-7.2)	n=16	6	(4.9-6.9)	n=9	7.0	n=1
2 $\sigma$	0.5			0.3			0.3			0.4	0.4

#### 5.4. Zircon REE/trace element data

REE and trace element analyses were carried out on seven of the ten Etive samples (MO, Cr-11, Cr-15, Cr-26, St-05, St-01, Q-23). Etive zircons show the same features (HREE enrichment, positive Ce/Ce\* and negative Eu/Eu\*) as the Lochnagar zircons, but the variation between and within samples is even less pronounced (Fig. 12). The highest concentrations of REEs occur in zircons of the Cruachan and Quarry intrusions, and the lowest in zircons of the Starav Intrusion. Eu/Eu\* range from 0.22 in Quarry Intrusion sample Q-23 to 0.52 in Cr-15 of the Cruachan Intrusion.

#### 5.5. Zircon oxygen isotope data

Zircons of the Etive pluton have a mean  $\delta^{18}\text{O}$  value of  $6.5 \pm 0.4$  ‰ ( $2\sigma$ ,  $n=209$ ), which is essentially the same as that of the Lochnagar zircons. Again, each sample displays a different mean composition, range in  $\delta^{18}\text{O}$  and data distribution (Fig. 13a-j). Sample Q-25 of the Quarry Intrusion has the lowest mean  $\delta^{18}\text{O}$  ( $6.0 \pm 0.3$  ‰ ( $2\sigma$ )); Cr-11 of the Cruachan Intrusion, and St-05 and St-01 of the Starav Intrusion have the highest mean  $\delta^{18}\text{O}$  values ( $6.9 \pm 0.4$ - $0.5$  ‰ ( $2\sigma$ )). Thus, no systematic differences in mean oxygen isotope composition can be observed between facies.

Some systematic differences occur in the range of values and distribution patterns. All samples of the Starav Intrusion (St-01, St-05, St-06) show the least variation with data ranges of 1.1 ‰ (St-01: 6.3-7.4 ‰) to 1.4 ‰ (St-06: 5.6-7.0 ‰) and unimodal to weakly bimodal (St-01) distributions. The largest heterogeneities can be observed in the Meall Odhar Intrusion sample (2.7 ‰), and in samples of the Cruachan Intrusion (except Cr-15). Cr-17 displays a 3 ‰ range between 4.6-7.6 ‰, which falls into three modes. Similarly, sample Cr-11 has two dominant and one less pronounced mode. All other Etive samples display unimodal to bimodal distributions.

As in zircons of the Lochnagar pluton, the large variation in oxygen isotope composition within samples largely results from differences in  $\delta^{18}\text{O}$  between zircon

crystals. However, resolvable intra-grain variations (both increase and decrease with zircon growth) may be observed in the Meall Odhar Intrusion, Cr-11, Cr-17 and Cr-26 of the Cruachan Intrusion and Q-23 of the Quarry Intrusion.

The inherited components found in the Cruachan Intrusion give oxygen isotope values of  $6.2 \pm 0.4\text{‰}$  (n=1) for Cr-17 and  $5.9 \pm 0.4$  (n=1) and  $7.0 \pm 0.4$  (n=1) for Cr-15.

## 6. Discussion

### *6.1. Age data and emplacement histories of the Lochnagar and Etive plutons*

TIMS age dating of the main Lochnagar pluton facies L1, L2 and L3 suggested that L1 and L2 were emplaced approximately contemporaneously at  $425 \pm 4$  Ma (zircon age) and L3 somewhat later at  $417 \pm 1$  Ma (monazite age) (Smith et al., 2001). Based on cross-cutting field relationships the diorites were interpreted to be older than the Lochnagar granite facies (Smith et al., 2001). Our new U-Pb SIMS zircon data are in good agreement with the published ages of L1 and L2 (SIMS data:  $424 \pm 5$  Ma to  $419 \pm 4$  Ma). However, the SIMS age for L3 of  $423 \pm 2$  Ma is at least 3 m.y. older than that reported by Smith et al. (2001). As L3 intrudes L1 in at least five different locations, it may be that not all of these locations actually belong to L3 and therefore differ in age. Two of the diorite samples, AD1 and CnG, intruded broadly contemporaneously with the main granite body at  $419 \pm 2$  Ma and  $418 \pm 3$  Ma, while the second sample of the Allt Darrarie diorite (AD2) was emplaced somewhat later at  $413 \pm 4$  Ma. Hence, the Allt Darrarie diorite was assembled in at least two separate magma batches – the first batch prior to or contemporaneously with L1, L2 and L3 and the second batch later than the main granite body. Based on these ages the emplacement history of the pluton is more complicated than previously assumed and magmatic activity lasted for approximately 11 m.y..

Based on field relationships the Etive pluton intruded from the rim to the centre in the following sequence: Quarry Intrusion, Cruachan Intrusion, Meall Odhar Intrusion, Starav Intrusion (Bailey, 1960). Published Rb-Sr, Ar-Ar and K-Ar ages

range from 410 Ma to 373 Ma (Brown, 1975; Brown et al., 1968; Clayburn, 1981; Clayburn et al., 1983; Halliday et al., 1979; Harmon and Halliday, 1980; Pankhurst, 1982), while U-Pb zircon TIMS dating by Pidgeon and Aftalion (1978) gave ages of 405 Ma and  $390 \pm 6$  Ma. Based on these ages Clayburn et al. (1983) concluded that the Etive Complex was emplaced approximately contemporaneously at 400 Ma. However, more recently Morris et al. (2005) obtained Ar-Ar biotite ages of  $415 \pm 1.8$  Ma and  $414 \pm 2$  Ma for the Etive dyke swarm, which they interpreted to mark the end of magmatism in the Etive pluton, indicating that the pluton is at least 15 m.y. older than previously assumed.

The SIMS U-Pb zircon ages from this study do not agree with the published data. Our data show that the Etive pluton intruded over a period of approximately 16 m.y. between  $423 \pm 2$  Ma and  $407 \pm 3$  Ma (or  $405 \pm 29$  Ma). Hence the earliest phases of the pluton are much older and the end of magmatic activity in the area was at least 10 m.y. later than proposed by Morris et al. (2005). The emplacement sequence also differs from the published data insofar as the Meall Odhar Intrusion ( $423 \pm 2$  Ma) and Cr-11 ( $421 \pm 5$  Ma) of the Cruachan Intrusion represent the oldest phases in this study. This is followed by the remaining samples of the Cruachan Intrusion, which were emplaced between  $414 \pm 6$  Ma and  $413 \pm 6$  Ma. This is consistent with our observed field relationships between the Cruachan and Meall Odhar intrusions.

Contemporaneously and subsequently the Starav Intrusion ( $412 \pm 6$  Ma to  $403 \pm 2$  Ma) and the marginal Quarry intrusion ( $408 \pm 3$  Ma) were emplaced. Thus, the main part of the pluton was emplaced from the rim inwards, but in the final stage intrusion also occurred along its fringes.

This detailed U-Pb zircon SIMS study of the Lochnagar and Etive plutons demonstrates that both plutons have much longer and more complicated emplacement histories than previously assumed. Some facies (e.g. Lochnagar: Allt Darrarie diorite, Etive: Cruachan Intrusion) appear to comprise two or more magma batches, which may have assembled incrementally to form the plutons.

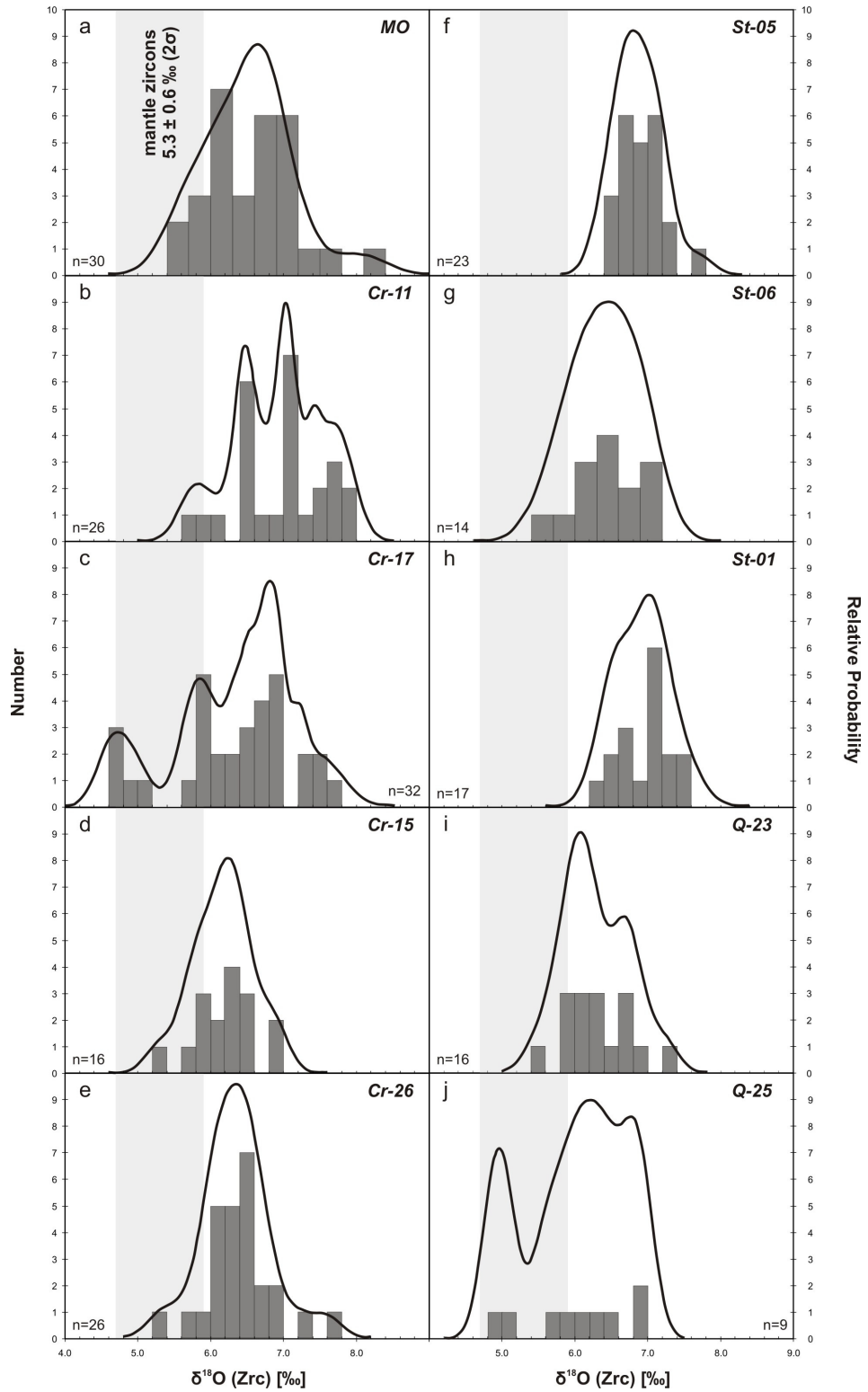


Fig. 13: Oxygen isotope probability-histograms of zircons of the Etive pluton (bin width =  $1\sigma$ , probability curves were calculated at  $1\sigma$ ).

## 6.2. *Crustal recycling vs. crustal growth*

Oxygen isotope compositions of whole-rocks and zircons are commonly used to distinguish between mantle and crustal origins. As oxygen isotopes fractionate more strongly with decreasing temperature and  $\delta^{18}\text{O}$  increases with increasing  $\text{SiO}_2$  content, the crust is more enriched in  $^{18}\text{O}$  than the mantle. Studies of zircons from mantle-derived xenoliths in kimberlites have demonstrated that mantle reservoirs display a narrow range of oxygen isotope compositions of  $5.3 \pm 0.6 \text{‰}$  (Valley et al., 1998). The oxygen isotope compositions of zircons in granitic rocks are a key indicator of their sources (pristine mantle, lower and/or middle crustal (infracrustal), and supracrustal sources). Recently, this approach has gained importance in crustal growth studies, which have attempted to quantify the extent to which I-type granites represent the growth of new crust versus the recycling of pre-existing lower crust. A study by Kemp et al. (2007) has demonstrated that up to 85 % new crust was generated during formation of the Lachlan Fold Belt I-type granites.

Zircon crystals yield oxygen isotope compositions of  $5.3\text{--}8.1 \pm 0.6 \text{‰}$  (mean= $6.6 \text{‰}$ ) in the Lochnagar pluton and  $4.6\text{--}8.2 \pm 0.4 \text{‰}$  (mean= $6.5 \text{‰}$ ) in the Etive pluton. The vast majority of zircon  $\delta^{18}\text{O}$  values in both plutons (c. 82 %) lie outside the  $\delta^{18}\text{O}$  range for mantle zircons ( $5.9 \text{‰}$ ). In the Lochnagar pluton zircons with mantle-like  $\delta^{18}\text{O}$  signatures predominantly occur in the Cul nan Gad diorite, where they comprise c. 58 % of the data set. All other samples contain only rare zircon crystals with mantle-like signatures, representing low-  $\delta^{18}\text{O}$  outliers within their populations. Overall, none of the samples contain entire zircon populations with  $\delta^{18}\text{O}$  values expected from mantle zircons.

In the Etive pluton samples of the Cruachan Intrusion contain the highest proportion of mantle-like zircons; sample Cr-17 contains a small but distinct sub-population of five mantle-like zircons (out of 32). However, as in the Lochnagar pluton, all other samples comprise only few or no mantle-like zircons, and these represent the low- $\delta^{18}\text{O}$  tails of higher- $\delta^{18}\text{O}$  populations.

The oxygen isotope compositions of zircons are essentially unaffected by fractional crystallisation and hydrothermal alteration; a change in  $\delta^{18}\text{O}$  can only be achieved by open-system processes such as magma mixing or assimilation (Valley,

2003). Thus, our data suggest that both plutons contain only a very small distinct and pristine mantle-derived component. The vast majority of zircons grew from melts that had either experienced magma mixing or assimilation of higher- $\delta^{18}\text{O}$  components prior to zircon crystallisation, or were derived by melting of infracrustal source rocks enriched in  $^{18}\text{O}$  relative to mantle values. The occurrence of minor amounts of inherited zircon and magmatic zircons with  $\delta^{18}\text{O}$  values of up to  $8.2 \pm 0.5$  ‰ in the Lochnagar and Etive plutons indicates that assimilation of a supracrustal component such as the surrounding Dalradian country-rocks is possible.

Due to lack of outcrop the mantle and crustal components present underneath the Grampian Highlands are not well constrained. In order to explain the zircon  $\delta^{18}\text{O}$  values observed in the Lochnagar and Etive plutons we carried out simple two-component magma mixing modelling involving the two most obvious end-members, i.e. a mantle component ( $\delta^{18}\text{O} = 5.5$  ‰) and the Dalradian Supergroup country rocks (average  $\delta^{18}\text{O} = 14.2$  ‰). According to this model the Lochnagar and Etive plutons comprise 70-100 % mantle and 0-30 % of a Dalradian-like supracrustal component. This would suggest that the Lochnagar and Etive plutons, like the Lachlan Fold Belt I-type granites (Kemp et al., 2007), were predominantly derived from the mantle, hence played an important role in Phanerozoic crustal growth. However, several facts suggest that a more complex petrogenetic evolution model for the Lochnagar and Etive plutons a scenario involving other infra- and/or supracrustal sources appears more realistic. (1) Field observations show that country rock xenoliths are rare and generally undigested in the plutons indicating late-stage assimilation during emplacement. (2) Whole-rock geochemical and isotopic data of the Lochnagar and Etive plutons are complex and differ from each other suggesting involvement of different sources. (3) Zircon  $\delta^{18}\text{O}$  values vary between plutons, samples of a single pluton, crystals of a single sample and even within individual zircon crystals providing strong evidence for a complex petrogenetic evolution. As based on oxygen isotope data alone, it is impossible to identify and decipher between these unknown crustal sources the role and importance of the late Caledonian I-type granites in crustal growth cannot be unambiguously assessed.



### *6.3. Evidence for magma mixing*

A striking feature of the oxygen isotope data for zircons of the Lochnagar and Etive plutons is the heterogeneity between samples of the same facies, within single samples (e.g. Lochnagar: AD1, Etive: Cr-17) and within individual crystals. As the degree of heterogeneity within these samples is much larger than in zircon standard 91500 analysed in the same analytical session, these variations cannot be the result of differences in instrument performance. Furthermore, as all dubious data were rejected from the data sets, we interpret these variations to reflect real compositional changes in the magmas from which the zircons crystallised.

Detailed examination of each zircon crystal has shown that variations in  $\delta^{18}\text{O}$  do not correlate with zircon morphologies or CL zoning. Heterogeneities predominantly occur between crystals. However, some samples, mostly from the Cruachan Intrusion, contain individual zircon crystals that show large resolvable variations in  $\delta^{18}\text{O}$ . These variations are not systematic and are not spatially related to resorption surfaces; they occur between cores and rims, between different core domains and commonly even within a single zone. A further observation is that  $\delta^{18}\text{O}$  values increase as well as decrease with zircon growth in zircons from an individual sample. The same pattern has been described for zircons of the Lochnagar Allt Darrarie diorite (AD1), where it has been proposed that the diorite is the product of mixing of several melt batches of differing oxygen isotope composition, which mixed before and during zircon growth (Paper 1). Our detailed study of the Lochnagar and Etive plutons indicates that this pattern of  $\delta^{18}\text{O}$  variation in zircons is not peculiar to the Allt Darrarie diorite. Similar magma mixing processes to those deduced for the Allt Darrarie diorite are characteristic of the majority of samples of both plutons.

### *6.4. Petrogenetic model*

The application of new and more precise analytical techniques such as those employed in this study now permit fundamental questions about granite genesis, ascent and emplacement remain to be addressed more rigorously. Plutons were believed to represent large bodies of siliceous magma generated either by fractional

crystallisation of mantle-derived basalt or basaltic andesite in shallow crustal magma chambers (e.g. Grove et al., 1997; Pichavant et al., 1992; Sisson and Grove, 1993) or close to the Moho (e.g. Annen and Sparks, 2002; Mortazavi and Sparks, 2003; Müntener et al., 2001; Prouteau and Scaillet, 2003), or by dehydration melting in the lower or middle crust induced by intrusion of hot, hydrous, mafic, mantle-derived magma (e.g. Jackson et al., 2003; Petford and Atherton, 1996; Smith and Leeman, 1987). After formation they were thought to ascend rapidly by diapirism or stoping to shallower emplacement levels (e.g. Buddington, 1959; Paterson et al., 1996; Petford et al., 2000; Pitcher and Berger, 1972). However, these models are problematic for the following reasons: (1) seismic techniques have only rarely been able to locate large molten magma bodies (e.g. Detrick et al., 1990); (2) thermal modelling has demonstrated that it is difficult to maintain even small permanent magma chambers (e.g. Lister, 1983), and (3) it has been shown that diapiric ascent of magma is too slow and energetically inefficient to be geologically important (e.g. Clemens and Mawer, 1992; Petford et al., 2000).

Recent thermal models suggest that ‘deep crustal hot zones’ may play an important role in the generation of intermediate and silicic igneous rocks (Annen et al., 2006; Annen and Sparks, 2002). The development of deep crustal hot zones results from repeated intrusion of mantle-derived hydrous basalt sills into the lower and/or middle crust, where melts are generated either by differentiation of the basalt sills to produce residual and more siliceous H<sub>2</sub>O-rich melts or by partial melting of pre-existing crustal rocks including early basalt sills or older mafic lower crust. Mixing of residual melts (or mafic mantle melts) and crustal partial melts creates a large range of intermediate and silicic melts. Depending on their H<sub>2</sub>O content and ascent path, these melts will ascend more or less rapidly into a shallow reservoir in the upper crust where they undergo crystallisation by degassing and cooling. Thus, chemical diversity is primarily acquired at depth and textural diversity at shallow levels (Annen et al., 2006).

The ‘deep crustal hot zone’ model is in good agreement with field and geochronological evidence, which suggests that some (and perhaps most) plutons were emplaced incrementally as a series of sheet-like or dyke-like intrusions over time spans an order of magnitude longer than the thermal lifetime of large magmatic

masses and never existed as a large molten magma body (Brown and McClelland, 2000; Coleman et al., 1995; Wiebe, 1993; Wiebe and Collins, 1998). For example, TIMS dating of the Tuolomne Intrusive Suite in California provided evidence for incremental assembly over a period of at least 10 m.y. (Coleman et al., 2004). Contacts between different granite facies may be sharp, gradational or cryptic depending on the time between injection events and the degree of homogenisation by post-emplacement annealing (Glazner et al., 2004). Hence, the chemical heterogeneity previously interpreted to result from fractional crystallisation (e.g. Bateman and Chappell, 1979; Sisson and Moore, 1994; Tindle and Pearce, 1981) and/or magma mixing (Frost and Mahood, 1987; Kistler et al., 1986) in large magma chambers, actually reflects processes operating at much deeper levels (Glazner et al., 2004), for example in deep crustal hot zones.

The Lochnagar and Etive plutons both comprise a range of magma compositions varying between gabbro-diorite and alkali-granite, consistent with formation in a deep crustal hot zone. The majority of zircons of the Lochnagar and Etive plutons show values more enriched in  $^{18}\text{O}$  than expected for mantle-like zircons ( $5.3 \pm 0.6 \text{ ‰}$  (Valley et al., 1998)), and hence crystallised either from melts that were produced by magma mixing between mantle melts and infra- and/or supracrustal melts, or solely from lower crustal or mid-crustal partial melts. Simple closed-system fractional crystallisation from a basaltic end member can be precluded as neither the Lochnagar nor the Etive pluton comprises populations of zircons with pristine mantle  $\delta^{18}\text{O}$  signatures. Assimilation and fractional crystallisation may explain the zircon oxygen isotope composition of the homogeneous samples (e.g. CnG diorite, Starav Intrusion). However, the majority of samples display resolvable oxygen isotope variations between and even within individual crystals, which indicates a more complex mixing or assimilation scenario involving several sources. Where resolvable differences in zircon  $\delta^{18}\text{O}$  between cores and rims were detected, increases as well as decreases in  $\delta^{18}\text{O}$  with zircon growth were observed, demonstrating that mixing between magma batches also occurred during growth, probably during ascent and at emplacement level. SIMS dating has revealed a range of U-Pb ages for zircons from the Lochnagar and Etive plutons. The  $^{18}\text{O}/^{16}\text{O}$  and U-Pb data together support a model of incremental granite and diorite assembly over extended periods of time (c.

11 m.y. at Lochnagar and c. 16 m.y. at Etive). In both plutons, few sharp contacts have been identified in the field; while this may be in part due to poor outcrop quality, it is probably also due to textural homogenisation of magma batches after emplacement.

Inherited zircons in the Lochnagar and Etive plutons give U-Pb ages similar to detrital zircons found in the Dalradian country rocks, possibly suggesting assimilation. However, since the identity of the basement beneath the Grampian Highlands remains speculative, more precise interpretation of the origins of the inherited zircon cores is not yet possible.

#### *6.5. Comparison of the Lochnagar and Etive plutons*

Whole-rock geochemical data from the Cairngorm and Argyll suites (Fowler et al., 2001; Halliday, 1984; Halliday et al., 1985; Stephens and Halliday, 1984; Tarney and Jones, 1994; Thirlwall, 1988) display several compositional differences such as enrichment in the majority of trace elements and REEs in the Cairngorm Suite plutons relative to the Argyll Suite plutons (Fowler et al., 2001; Halliday, 1984; Halliday et al., 1985; Stephens and Halliday, 1984; Tarney and Jones, 1994; Thirlwall, 1988). This has been interpreted to reflect either compositional variations between their crustal and mantle sources, and/or differences in the relative crust and mantle contributions (Halliday, 1984).

Similarly, zircons show on average higher REE and trace element abundances in the Lochnagar than in the Etive pluton. This may be evidence that the sources that contributed to the Lochnagar pluton were more enriched than those of the Etive pluton. However, as REE abundances in zircon vary at an inter- and intra-grain scale (between c. 250 ppm to 5000 ppm) (e.g. Black et al., 1986; Chen and Williams, 1990), the processes that control the incorporation of trace elements and REEs into zircon are not well constrained and little information is known about how much the zircon chemistry is affected by crystallisation conditions and the overall growth environment (e.g. Guo et al., 1996; Hinton and Upton, 1991), the usefulness of REE and trace element concentrations in zircon as petrogenetic indicators is limited (Hoskin and Schaltegger, 2003).

The other difference between the plutons is the range of ages of inherited zircons. The L2 facies of the Lochnagar pluton contains inherited zircons ranging from 1.4 Ga to 1.05 Ga, whereas in the Cruachan Intrusion (Etive pluton) ages range from 1.65 Ga to 1.05 Ga. This may suggest that the basement beneath the Etive pluton contains older components, but due to the ambiguities that surround the origin of inherited zircons, this cannot be treated as unequivocal.

No other systematic characteristics were observed that help to explain the two plutons' distinct whole-rock compositions. Rather, zircon U-Pb and oxygen isotope data have identified a number of commonalities between them: (1) Both show a range of U-Pb ages and heterogeneous  $\delta^{18}\text{O}$  distributions within and between samples, providing strong evidence for incremental pluton assembly; (2) The ranges and means of zircon  $\delta^{18}\text{O}$  distributions and their absolute values are within error the same in both plutons, and indicate a similarly small proportion of zircons with mantle-like values. The plutons probably comprise a similar mix of sources consisting of pristine mantle, lower crust and/or middle crust and possibly of Dalradian country rocks; (3) The degree and scale of heterogeneity in  $\delta^{18}\text{O}$  is the same within the plutons. Variation occurs between granite facies, within the same facies, between samples, between zircon crystals of a single sample and also within individual crystals. However, both plutons also contain homogeneous samples. These are source heterogeneities that are potentially produced in a 'deep crustal hot zone'.

In summary, the relative source contributions and the processes with respect to melt generation, ascent and emplacement were probably the same for the Lochnagar and Etive plutons, and hence cannot be responsible for the whole-rock geochemical differences between the plutons. We conclude that the latter are therefore probably the result of compositional differences between the plutons' infracrustal and/or mantle sources.

#### *6.6. Implications for future granite studies*

This study has provided detailed new insights into the complexity of plutonic systems and processes. Plutons are mapped, subdivided into facies and interpreted based on field evidence, petrographic, whole-rock geochemical and isotopic data.

More recently, zircon data have been obtained by single- and/or multi-grain techniques and now by in-situ techniques; these have provided a basis for major progress towards identifying and quantifying granite sources (e.g. Kemp et al., 2007), and ascent and emplacement mechanisms (Coleman et al., 2004; Glazner et al., 2004). Samples are commonly selected from the main facies on the basis of interpretations of geological mapping and petrographic description. The U-Pb and  $^{18}\text{O}/^{16}\text{O}$  heterogeneities that are evident at various (intra-grain to hand specimen to pluton) scales amongst the zircon populations in this study call into question whether any one sample collected from a granitic pluton can ever be considered to be representative of an entire pluton. Based on in-situ high-precision oxygen isotope and U-Pb analysis we have been able to demonstrate that the degree and scales of heterogeneity that have been identified are much greater than can be resolved by conventional analytical methods. This raises two fundamental questions: (1) What do granite facies within plutons really reflect and how should they be interpreted? Our study suggests that even small intrusions such as the Allt Darrarie diorite of the Lochnagar pluton (dimensions: 0.6 x 0.4 km) comprise several magma batches, which may vary in their geochemical and isotopic characteristics. Evidence for this may be found in the two Allt Darrarie samples AD1 and AD2, which differ in age (AD1:  $419 \pm 2$  Ma, AD2:  $413 \pm 4$  Ma), mean oxygen isotope composition (AD1:  $7.1 \pm 0.4$  ‰, AD2:  $6.6 \pm 0.5$  ‰), range of  $\delta^{18}\text{O}$  values (AD1: 6.1-8.1 ‰, AD2: 5.9-7.5 ‰) and in  $\delta^{18}\text{O}$  data distribution (AD1: bimodal, AD2: unimodal). (2) How representative are the results of many traditional granite studies, especially when undertaken on a very small number of samples?

The philosophy underlying these questions was addressed by Krauskopf (1968) in his “tale of ten plutons” from the Sierra Nevada batholith. He suggested that granite magmas form, ascend, differentiate and mix in an apparently random fashion making it impossible to establish a complete “stratigraphy” of intrusive units even if more precise data were available. On the one hand this is correct as the deeper we delve into the detail of granitic rocks the greater is the emerging complexity. On the other hand, the integration of new micro-analytical techniques applied to zircons and recent theoretical models have led to major progress in understanding and interpreting the complexity of granitic rocks. In the process new insights into the

mechanisms and processes of granite intrusion have been revealed, and much tighter and more quantitative constraints on their sources and on the role granites play in the generation and differentiation of the continental crust have been set.

## 7. Conclusions

1. The Lochnagar pluton intruded Dalradian metasedimentary country rocks between  $424 \pm 5$  Ma and  $413 \pm 4$  Ma (over c. 11 m.y.), and the Etive pluton intruded similar rocks between  $423 \pm 2$  Ma and  $407 \pm 2$  Ma (over c. 16 m.y.). The large ranges of U-Pb ages observed within the plutons suggest both were probably assembled incrementally and never existed as large molten bodies of magma.
2. Zircons of the Lochnagar and Etive plutons have the same mean oxygen isotope composition (Lochnagar:  $6.6 \pm 0.6$  ‰ ( $2\sigma$ ), Etive:  $6.5 \pm 0.4$  ‰ ( $2\sigma$ )) and the same proportion of mantle zircons (c. 18 %). This suggests that the relative mantle and crust contribution must have been similar in both plutons. The majority of zircons display oxygen isotope compositions that are more  $^{18}\text{O}$ -enriched than pristine mantle values, which indicates that the plutons are either the products mixing between mantle and infra- and/or supracrustal sources or of recycled infra- and/or supracrustal components. Simple two-component mixing between mantle-derived melts and supracrustal material (e.g. Dalradian Supergroup country rocks) appears to be too simplistic and fails to explain the zircon oxygen isotope variations observed in the Lochnagar and Etive plutons. From oxygen isotope data alone it is not possible to identify the unknown crustal sources, hence to quantify the amount of new crust in the plutons.
3. Most of the Lochnagar and Etive pluton samples show a large range in zircon  $\delta^{18}\text{O}$ . Heterogeneity in oxygen isotope composition occurs between and within facies, between samples, between zircon crystals of a single sample and even within individual zircons. In the latter case, an increase as well as decrease in  $\delta^{18}\text{O}$  with zircon growth can be observed, which may be interpreted as evidence of magma mixing between melts of differing oxygen isotope composition. This

degree of complexity and scale of heterogeneity has not previously been reported.

4. The complexity observed in the Lochnagar and Etive plutons supports melt generation in a 'deep crustal hot zone'. The observed geochemical and isotopic variations were in part produced by mixing of melts before zircon crystallisation, but also by subsequent mixing during zircon growth. Melts ascended as melt batches to shallower levels where they were incrementally assembled to form the plutons.
5. The processes and relative mantle vs. crust contributions appear to be similar in the Lochnagar and Etive plutons, and hence fail to explain their whole-rock geochemical differences. The only differences have been found in zircon trace element and REE data, which demonstrate that the Lochnagar zircons on average contain higher abundances than those of the Etive pluton. However, in general REE and trace elements in zircon have been found of limited use as petrogenetic indicators. In addition, U-Pb dating of inherited zircons has identified slightly older ages in the Etive pluton. However, this cannot be considered unambiguous evidence for older basement beneath the Etive pluton as detrital zircons found in the Dalradian country rocks also display these ages.



# **IV.**

## **PAPER 3**

**Using in-situ O and Hf isotope analysis of  
zircons to constrain the sources of late  
Caledonian granites in Scotland**

# Using in-situ O and Hf isotope analysis of zircons to constrain the sources of late Caledonian granites in Scotland

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## Abstract

Previous whole-rock geochemical and isotopic studies of the Scottish late Caledonian (~430-400 Ma) I-type granites produced controversial results regarding the contribution of crust and mantle sources to their genesis. In-situ oxygen and Hf isotope data of zircons from the Scottish Lochnagar and Etive plutons show that with  $\delta^{18}\text{O}$  (zircon) values of  $5.3\text{--}8.1 \pm 0.6 \text{‰}$  ( $2\sigma$ ) and initial  $\epsilon\text{Hf}$  values of  $+3.4$  to  $-5.8 \pm 1.0$  ( $2\sigma$ ), the Lochnagar pluton probably contains an enriched mantle component. Zircons from the Etive pluton display a similar range of  $\delta^{18}\text{O}$  values ( $4.6\text{--}8.2 \pm 0.4 \text{‰}$ ), but less radiogenic Hf isotope compositions ( $\epsilon\text{Hf} = -3.0$  to  $-10.6 \pm 1.0$ ), which make derivation from the mantle less plausible. Based on these data the Etive pluton, and possibly also the Lochnagar pluton, played an insignificant role in Phanerozoic crustal growth.

Large whole-rock compositional differences between the Lochnagar and Etive plutons have been interpreted to either reflect compositional variations between their sources or in the relative contributions of crust and mantle sources. This may now be resolved. The range of zircon oxygen and Hf isotope compositions identified in each pluton and the differences in  $\epsilon_{\text{Hf}}$  between the plutons indicate that the lower crust beneath the Grampian Highlands is very heterogeneous and comprises components of differing age and composition. Calculated Hf model ages show that the Lochnagar pluton has predominantly sourced lower crust of Mesoproterozoic age, and the Etive pluton crust of Palaeo- and Mesoproterozoic age. Thus, the whole-rock compositional differences predominantly reflect variations in the underlying crustal and mantle sources and not in the relative contributions of mantle vs. crust.

## 1. Introduction

Determining the relative contributions of mantle and crust in the genesis of granites has been the primary aim of many whole-rock geochemical and isotopic studies that have attempted to constrain the role of granite magmatism in the crust's evolution. 'I-type' granites (igneous or infracrustal precursors) (Chappell and White, 1974) have been of particular interest. Controversy persists over whether these are predominantly derived from the mantle, and thus actively contribute to growth of continental crust, or are the products of melting and recycling of pre-existing lower crust.

Traditionally, petrogenetic studies of granites have used geochemical and isotopic data derived from whole-rock samples. These deliver 'averaged' information for all minerals in the rock and are commonly affected by alteration. Therefore, they are unrepresentative of the magma composition at the time of crystallisation, which limits their usefulness in petrogenetic studies. Recent advances in in-situ microanalysis now enable access to the geochemical and isotopic information stored in zircons at high spatial resolution and analytical precision, providing insight into a previously inaccessible record of magma evolution. Zircon is a common accessory mineral in granitoid rocks. Its highly refractory nature allows individual crystals to retain a direct record of magma composition, and in many cases this record may span much of the magmatic history. In addition, older 'inherited' cores may be preserved, which yield age and compositional information about source rocks and assimilates. Changes in melt composition, temperature or crystallisation conditions arising from either local closed-system processes or large-scale open-system changes (e.g. magma mixing, assimilation) are recorded in concentric zircon growth zones (Hoskin and Schaltegger, 2003; Shore and Fowler, 1996; Vavra, 1990, 1993, 1994) and may be imaged by cathodoluminescence (CL) and back-scatter electron (BSE) imaging techniques. As zircon contains significant concentrations of U, Th, REEs (all ppm level) and Hf (percent level) (Kinny and Maas, 2003) it is suitable for oxygen, Hf and U-Pb isotope analysis, and trace element/REE analysis. The high spatial resolution of the ion microprobe enables oxygen and U-Pb isotope and REE/trace element data to be obtained on the same c. 20  $\mu\text{m}$  diameter spot. Subsequent in-situ

Hf isotope analysis by laser ablation (LA-MC-ICPMS), made on a c. 50  $\mu\text{m}$  diameter spot, can be positioned over the ion probe spots. This approach allows integration of the various data sets and correlation with textural information (e.g. comparisons of zircon cores and rims within and between crystals), and can hence be used to constrain: the emplacement ages of plutons (U-Pb data); the relative mantle and crustal contributions (REE, O and Hf isotope data); the crustal residence age(s) of the source(s) (Hf isotope data); and, based on the latter, the contribution of the magma to crustal growth. Collectively, these offer a major step forward in deciphering granite sources and petrogenetic histories.

A study applying this integrated approach has recently been carried out on zircons from I-type granite suites (Why Worry, Jindabyne and Cobargo suites) of the Lachlan Fold Belt (LFB) of southeastern Australia (Kemp et al., 2007). The data from that study, which indicate mixing between mantle-derived juvenile material and a supracrustal component, led to two important conclusions: (1) the I-type granites predominantly represent new crust and are therefore major contributors to continental growth, and (2) each granite magma comprises multiple sources.

The same integrated analytical approach is applied here to zircons from late Caledonian (~430-400 Ma) plutons emplaced in the Grampian block of the Scottish Highlands. Despite numerous studies utilising whole-rock data the origin of the late Caledonian I-type granites remains controversial. Most studies favour a mixed source origin comprising juvenile (mantle) and infracrustal components (Clayburn et al., 1983; Halliday, 1984; Halliday et al., 1979, 1980; Harmon and Halliday, 1980), which suggests they contributed to crustal growth. However, some authors propose that the plutons have predominantly recycled one or more infracrustal sources and experienced assimilation of a supracrustal component (Frost and O’Nions, 1985). We address this issue by integrating new in-situ Hf data with O and U-Pb data (Papers 1 & 2) from zircons in the late Caledonian Lochnagar and Etive plutons.

## 2. Geological background

### 2.1. The late Caledonian granites

The late Caledonian I-type granites were emplaced into mainly metasedimentary rocks of the Dalradian Supergroup in the Grampian Highlands of Scotland between c. 430 Ma and 400 Ma (Fig. 1) (Oliver, 2001; Rogers and Dunning, 1991; Stewart et al., 2001); the main phase of emplacement appears to have been at approximately  $425 \pm 5$  Ma (Fraser et al., 2004; Rogers and Dunning, 1991; Paper 2), broadly contemporaneously with the Scandian Event, involving the oblique collision of Baltica and Laurentia (Brown, 1991; Brown et al., 1985; Coward, 1990; Dallmeyer et al., 2001; Dewey and Mange, 1999; Kinny et al., 2003; Soper, 1986; Stephens and Halliday, 1984; Stephenson et al., 1999; Thirlwall, 1981, 1982, 1988). However, a robust genetic link between the Scandian Event and the voluminous I-type magmatism has yet to be established. Thus, the exact tectonic setting that led to emplacement of the late Caledonian I-type granites in Scotland is still controversial and several models exist. The favoured model linking the I-type granites to a subduction zone setting (Brown, 1991; Brown et al., 1985; Soper, 1986; Stephens and Halliday, 1984; Stephenson et al., 1999; Thirlwall, 1981, 1982, 1988) has recently been challenged by a slab-breakoff model (Atherton and Ghani, 2002).

The majority of late Caledonian I-type granites are hornblende bearing (Soper 1986), show a metaluminous affinity (except for granitoids with  $> 70$  wt%  $\text{SiO}_2$ , which are commonly peraluminous) (Frost et al., 2001), high Rb/Sr and K/Na, low K/Rb and relatively low initial Sr ratios (Halliday et al., 1985; Stephens, 1988; Thirlwall, 1988). Based on whole-rock geochemical and isotopic data the granites have been divided into three suites (Fig. 1) (Stephens and Halliday, 1984). The *Argyll suite* consists mainly of hornblende-biotite granodiorite and biotite granodiorite plutons, with some diorite and monzogranite; small intrusions of appinitic rock are commonly associated with the plutons (Stephens and Halliday, 1984; Strachan et al., 2002). The rocks are typically strongly metaluminous in comparison to those of the other suites, with high concentrations of Ba, Sr and Na, and low concentrations of Nb, Th and Rb (Fowler et al., 2001; Halliday, 1984;

Halliday et al., 1985; Stephens and Halliday, 1984; Tarney and Jones, 1994; Thirlwall, 1988). The *Cairngorm suite* consists of biotite monzogranite with minor granodiorite, and varies texturally between microgranite and coarse-grained, K-feldspar megacrystic granite. The intrusions contain high concentrations of Rb, Nb, Th and U, but have low Ba, Sr, Ti, P contents. Appinitic intrusions are essentially absent (Stephens and Halliday, 1984). The *South Grampians suite* is dominated by granodiorites and monzogranites, and has a higher proportion of gabbroic and appinitic intrusions. The suite is strongly metaluminous with higher K and Th abundances than the Argyll suite, but lower concentrations of Zr, La, Ce, Ba and Rb (Stephenson et al., 1999)

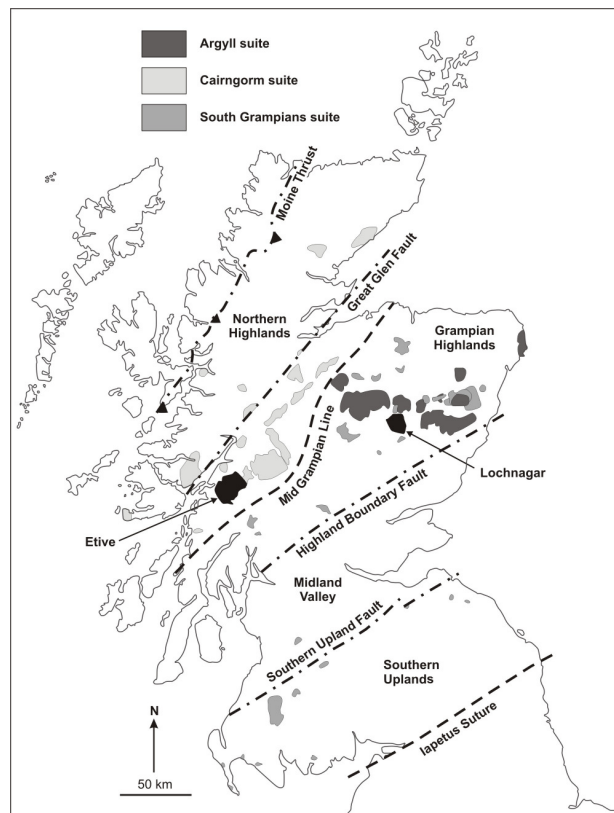


Fig. 1: Map of the late Caledonian granites and showing the locations of the target plutons Lochnagar and Etive (after Stephenson et al., 1999).

To date the reasons for the compositional differences between the suites are not fully resolved. However, it has been proposed that a major concealed discontinuity,

the Mid Grampian Line (MGL), separates Argyll suite plutons from the South Grampians and Cairngorm suite plutons (Fig. 1) (Halliday, 1984). As the whole-rock geochemical differences between the suites may reflect compositional variations in the lower crust beneath the Grampian block and/or variations in the composition and proportion of the mantle contribution to the melts, the MGL may represent an important boundary in the deep basement (Halliday, 1984) with some expression in the mantle. Supporting evidence has been found in inherited zircons, which show that plutons west of the MGL (i.e. in the Argyll suite) contain inherited cores that are older (c. 1600 Ma) than those in plutons to the east (Cairngorm suite) (c. 1100-1000) (Halliday, 1984). However, these ages have also been observed in detrital zircons from the surrounding Dalradian Supergroup (Cawood et al., 2003), which makes the origin of the inherited zircons ambiguous.

The basement onto which the Dalradian Supergroup was deposited is not exposed in the Grampian Highlands. However, based on exposures elsewhere in the surrounding region and in Ireland the Grampian terrane is conceivably underlain by the Lewisian Complex (c. 2.9 Ga), the Rhinns Complex (c. 1.8 Ga), Grenville-age basement (1.2-1.0 Ga) and/or rocks of the Dava and Glen Banchor successions (i.e. gneissose and locally migmatized psammite and semi-pelite with subordinate quartzite that were predominantly derived from Palaeoproterozoic- and Grenville-age sedimentary protoliths (Highton et al., 1999; Piasecki, 1980)).

## *2.2. The Lochnagar and Etive plutons*

### *2.2.1. The Lochnagar pluton*

The Lochnagar pluton, which is representative of the Cairngorm suite, crops out over an area of c. 150 km<sup>2</sup> and comprises three main granite facies (L1, L2, L3), microgranites and several marginal diorites (Fig. 2). The oldest part of the pluton is formed by L1, a circular pluton with a diameter of c. 15 km. It is commonly coarse-grained and inequigranular to porphyritic, and comprises plagioclase (39 %), K-feldspar (28 %), quartz (23 %), biotite (8 %) and hornblende (1 %). L1 was intruded by L2 (dimensions 12 x 9 km), which comprises mostly grey and pink medium- to coarse-grained, inequigranular to weakly porphyritic, unfoliated leucocratic rocks



that contain plagioclase (41 %), quartz (29 %), K-feldspar (26 %) and biotite (4 %). Both L1 and L2 granites were subsequently intruded by several pink quartz-K-feldspar-plagioclase-phyric microgranites, which are compositionally similar to their host granites. L3 granites are predominantly pink medium- to coarse-grained equigranular granites that contain K-feldspar (40 %), plagioclase (33 %), quartz (25 %) and biotite (2 %), and can be found in various locations within L1. As they have not been discovered in contact with L2, their relationship to L2 is unclear. Compositionally the L3 granites are much more evolved than L1 and L2, and hence may not be related to the main granite body (Smith et al., 2001). The marginal diorites (dimensions: 4-5 x 1.8 km (Cul nan Gad diorite) and 0.6 x 0.4 km (Allt Darrarie diorite) mostly consist of medium-grained, sometimes foliated, inequigranular quartz diorites containing plagioclase (38 %), hornblende and relict pyroxene (38 %), quartz (10 %), K-feldspar (7 %) and biotite (6 %). These were previously interpreted to be separate intrusive bodies that are related, but based on cross-cutting relationships older than the granite (Smith et al., 2001). However, new zircon REE and oxygen isotope data suggest that the diorites are part of the Lochnagar pluton (Paper 2). Thus, based on field relationships the order of intrusion is diorites, L1, L2, microgranite, L3 (Halliday, 1984; Halliday et al., 1979; Oldershaw, 1974; Smith et al., 2001).

Previous TIMS age data indicated that the Lochnagar pluton had a relatively simple emplacement history with intrusion of L1 and L2 approximately contemporaneously at c.  $425 \pm 5$  Ma (U-Pb zircon) and L3 some time later at c.  $417 \pm 1$  Ma (monazite age) (Smith et al., 2001). However, recent U-Pb zircon SIMS dating (Paper 2) showed that the Lochnagar pluton was emplaced incrementally over a period of c. 11 m.y. between  $424 \pm 5$  Ma and  $413 \pm 4$  Ma. At least one of the L3 granite intrusions was emplaced broadly contemporaneously with rather than subsequent to the L1 and L2 granites at  $423 \pm 2$  Ma. Furthermore, U-Pb dating detected that at least part of the Allt Darrarie diorite intruded after emplacement of the granites at  $413 \pm 4$  Ma. Hence the pluton has a much more complicated petrogenetic history than previously recognised.

There is little information on the sources that contributed to the Lochnagar pluton. Based on an  $\epsilon\text{Nd}_{415 \text{ Ma}}$  value of -2.7 and initial  $^{87}\text{Sr}/^{86}\text{Sr}$  values of 0.7063

( $n=1$ ), Halliday et al. (1984) proposed that the pluton comprises both mantle and crustal sources. Recent zircon oxygen isotope data have made a major contribution towards deciphering the pluton's sources and petrogenesis in more detail (Paper 2). Zircons from the Lochnagar pluton yielded a range of  $\delta^{18}\text{O}$  values between 5.3 ‰ and 8.1 ‰ and a mean of  $6.6 \pm 0.6$  ‰ ( $n=230$ ,  $2\sigma$ ). Thus, the majority of zircons (c. 82 %) show  $\delta^{18}\text{O}$  values more enriched in  $^{18}\text{O}$  than those of mantle-like zircons ( $5.3 \pm 0.6$  ‰ (Valley et al., 1998), but insufficiently  $^{18}\text{O}$ -enriched to have been derived from a solely supracrustal component. The presence of inherited cores in some zircons in the pluton is however consistent with a small supracrustal component such as the Dalradian Supergroup. Thus, based on these data the Lochnagar pluton appears to have been predominantly produced by (1) mixing between mantle-derived and infra- and/or supracrustal melts, or (2) recycling of pre-existing lower crust (Paper 2).

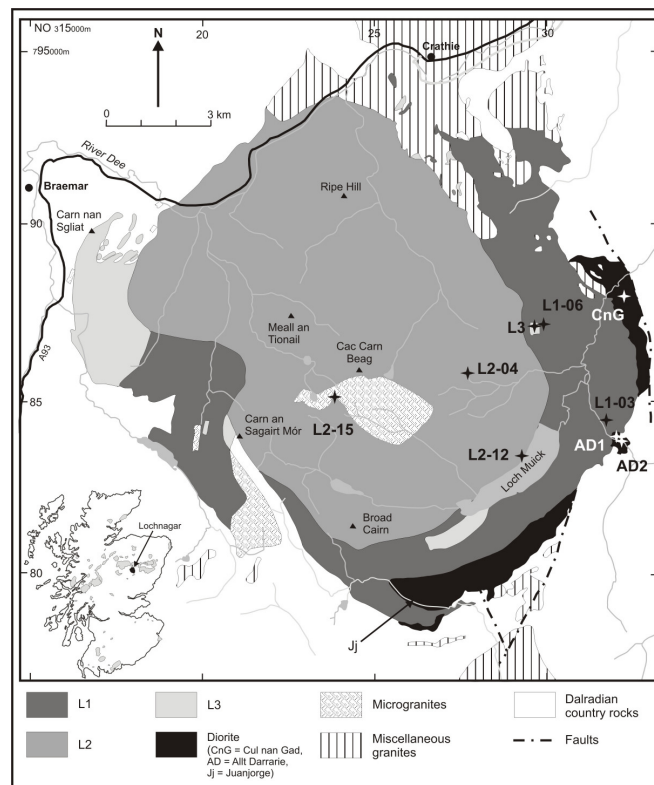


Fig. 2: Geological sketch map of the Lochnagar pluton with sample locations (Smith et al., 2001).

Oxygen isotope analysis of zircons has shown that the majority of samples display a range in zircon  $\delta^{18}\text{O}$  larger than expected from a homogeneous magma with variability occurring between samples, between crystals and even within individual crystals. This may be further evidence that the pluton represents an accumulation of a series of incrementally-assembled heterogeneous melt batches. Melts of differing  $\delta^{18}\text{O}$  are thought to have been generated in a deep crustal hot zone (Annen et al., 2006; Annen and Sparks, 2002; Papers 1 & 2). Mixing of melts probably occurred during ascent and also within a shallow magma chamber before final emplacement (Papers 1 & 2).

### 2.2.2. The Etive pluton

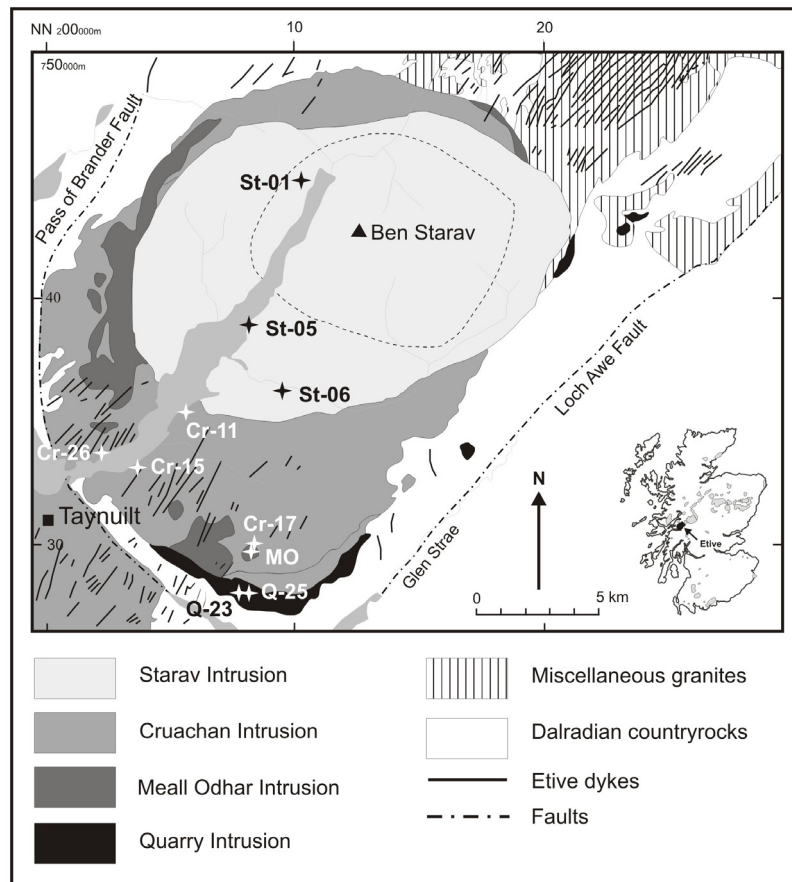


Fig. 3: Geological sketch map of the Etive pluton with sample locations (after Anderson, 1937; Batchelor, 1987).

The Etive pluton, which is representative of the Argyll suite, is exposed over an elliptical area of approximately 300 km<sup>2</sup> (Fig. 3). It is a major composite pluton comprising four main intrusive phases ranging in composition from granite to monzodiorite/diorite. Like the Lochnagar pluton, it has a predominantly calc-alkaline composition with the silicic phases showing a peraluminous and the more mafic phases a metaluminous affinity.

The Quarry Intrusion represents the outermost phase of the pluton and intruded as a small lens of granodiorite to diorite/quartz-diorite (Clayburn et al., 1983; Paper 2) containing country rock xenoliths and microdioritic or appinitic enclaves. Rocks of the Quarry Intrusion are commonly dark-grey, medium- to coarse-grained and plagioclase- or pyroxene-phyric, and contain plagioclase (46 %), hornblende (20 %), quartz (12 %), biotite (12 %) and pyroxene (9 %) (Batchelor, 1987). The largest part of the pluton is concealed by the compositionally heterogeneous Cruachan Intrusion, which ranges from granite through tonalite/granodiorite to monzodiorite and contains microgranitoid enclaves (Jacques and Reavy, 1994). The Cruachan Intrusion has been divided into two main varieties. In the northern lobe of the intrusion pale-grey, medium-grained, equigranular monzogranites are exposed, which contain occasional mafic clusters and metasedimentary xenoliths and comprise plagioclase (30-46 %), K-feldspar (23-34 %), quartz (16-28 %), biotite (4.5-6.5 %) and hornblende (3-9.5 %). The southern lobe comprises grey, medium- to fine-grained, equigranular monzodiorites, which show higher abundances of plagioclase (54-63 %) and often biotite (6-21 %), but only interstitial K-feldspar (7-25 %) and less quartz (5-12 %) (Batchelor, 1987). The Meall Odhar Intrusion has been described as a pink K-feldspar and quartz granite sheet and dyke intrusion, which cross-cuts all the earlier phases. However, field work carried out for this study has revealed numerous locations where the Cruachan Intrusion has intruded the Meall Odhar Intrusion. Similar to the other facies, it is compositionally variable and comprises fine- to medium-grained syenogranites and monzogranites (Stephenson et al., 1999). Syenogranites contain K-feldspar (50-67 %), quartz (27-37 %) and only small amounts of plagioclase (4.5-12 %) and hornblende (0.2-2 %), whereas monzogranites comprise quartz (30-42 %), K-feldspar (33-41 %), plagioclase (20-28 %) and biotite (0.5-1 %) (Batchelor, 1987). The centre of the Etive pluton contains the elliptical

Starav Intrusion, consisting of two concentric intrusions, which have been interpreted to represent at least two separate magma pulses. (Batchelor, 1987; Clayburn et al., 1983; Jacques and Reavy, 1994). The Outer Starav Facies is a medium- to coarse-grained K-feldspar- and hornblende-phyric syenogranite containing K-feldspar (27-46 %), plagioclase (23-41 %), quartz (21-32 %), biotite (3-6 %) and hornblende (0.2-6 %). Rocks of the Inner Starav Facies are medium-grained and equigranular. Compositionally they are similar to the Outer Starav Facies with the exception of higher abundances of quartz (28-40 %) and the absence of hornblende (Batchelor, 1987). To summarise, based on field relationships the pluton becomes younger towards the centre with the order of emplacement being Quarry Intrusion, Cruachan Intrusion and Starav Intrusion (Bailey, 1960). The Meall Odhar Intrusion probably intruded broadly contemporaneously with the Cruachan Intrusion.

Early radiometric dating of the pluton by Rb-Sr, Ar-Ar, K-Ar and U-Pb zircon TIMS methods delivered ages ranging from 410 Ma to 373 Ma (Brown, 1975; Brown et al., 1968; Clayburn, 1981; Clayburn et al., 1983; Halliday et al., 1979; Harmon and Halliday, 1980; Pankhurst, 1982; Pidgeon and Aftalion, 1978). Based on these dates Clayburn et al. (1983) concluded that the constituent parts of the Etive Complex were emplaced approximately contemporaneously at 400 Ma. However, more recently Morris et al. (2005) obtained Ar-Ar biotite ages of  $415 \pm 1.8$  Ma and  $414 \pm 2$  Ma for the Etive dyke swarm, which they interpreted to mark the end of magmatism. New U-Pb zircon SIMS data (Paper 2) indicate that the pluton, like Lochnagar, intruded over an extended time period of approximately 16 m.y., between  $423 \pm 2$  Ma and  $407 \pm 3$  Ma rather than contemporaneously. Based on these data, magmatic activity started with intrusion of the Meall Odhar Intrusion and parts of the Cruachan Intrusion, which was followed by the remaining phases of the Cruachan Intrusion, and ended with emplacement of the Starav Intrusion in the pluton's centre and the Quarry Intrusion along its outer margin.

The Nd and Sr isotope composition of the Etive pluton has been determined in more detail than the Lochnagar pluton, and data exist for all intrusive phases. All have negative  $\epsilon\text{Nd}_{400 \text{ Ma}}$  values ranging from -4.7 to -9.3 with the Cruachan Intrusion displaying the least negative and the Starav Intrusion and one sample of the Quarry Intrusion displaying the most negative values (Frost and O'Nions, 1985). Initial

$^{87}\text{Sr}/^{86}\text{Sr}$  values range from 0.7043 to 0.7068. Based on the Nd isotope data the Etive pluton contains a larger crustal component than the Lochnagar pluton, although Sr isotope data do not support this. Clayburn et al. (1983) proposed that the Etive pluton is the result of melting of both lower crustal and mantle components. The different phases are assumed to be derived from the same source, with the later phases such as the Starav Intrusion containing a larger crustal component (Clayburn et al., 1983). At present, the nature of the crustal component and the individual mantle and crustal proportions that have been involved in the generation of the Etive pluton remain unresolved.

Zircon oxygen isotope analyses of the Etive pluton gave a similar result to the Lochnagar pluton.  $\delta^{18}\text{O}$  values span a similar range from  $4.6 \pm 0.4\text{‰}$  up to  $8.2 \pm 0.4\text{‰}$  ( $2\sigma$ ,  $n=209$ ) with a mean value of  $6.5 \pm 0.4\text{‰}$  (Paper 2). Again c. 82 % of zircons yielded  $\delta^{18}\text{O}$  values too high for mantle-like zircons ( $5.3 \pm 0.6\text{‰}$  (Valley et al., 1998) but too low for supracrustal sources. Thus, the Etive pluton also appears to comprise a small pristine mantle component and multiple crustal sources (Paper 2). The degree of heterogeneity observed within individual samples and crystals is similar and in some samples of the Cruachan Intrusion, in particular, even greater than in zircons of the Lochnagar pluton, which suggests that the pluton has a very similar petrogenetic and intrusion history to the Lochnagar pluton (Paper 2).

### 3. Samples

Zircons from eight representative Lochnagar samples (AD1, CnG, L1-03, L1-06, L2-04, L2-12, L2-15, L3) and from nine Etive samples (MO, Cr-11, Cr-17, Cr-15, Cr-26, St-05, St-01, Q-23 and Q-25) were selected for in-situ Hf isotope analysis. Zircons from the Lochnagar and Etive plutons are broadly similar, displaying features typical of igneous zircon such as euhedral grain shapes, and oscillatory and/or sector zoning (Benisek and Finger, 1993; Hanchar and Miller, 1993; Hoskin and Schaltegger, 2003; Vavra, 1990). Each sample covers a range of grain sizes, morphologies (equant to acicular), zoning patterns and CL intensities and contains at least one and commonly multiple overgrown resorption surfaces. Resorbed cores

may comprise ~95 % of a crystal and are commonly overgrown by multiple rims. Cores are often weakly luminescent in CL, and are either entirely unzoned or consist of an inner unzoned domain and an outer oscillatory zoned domain. Some crystals, which predominantly occur in the more mafic phases of intrusion, contain only a very small unzoned core domain or lack it entirely. For a more detailed description of the zircons see Paper 2.

## **4. Methodology**

### *4.1. Whole-rock analyses*

REEs and some trace elements were analysed at the British Geological Survey (BGS) in Nottingham. The samples were fused with  $\text{Na}_2\text{O}_2$  and then leached with deionised water and HCl before analysis using a ThermoElemental PQ Excel quadrupole ICP-MS. Matrix-matched calibration standards were used throughout.

### *4.2. Zircon sample preparation*

Zircon separation was carried out in the University of St. Andrews Mineral Separation Facility. Rock samples of approximately 5 kg were crushed and sieved to obtain the < 500  $\mu\text{m}$  fraction from which zircon crystals were separated using a Wilfley Table, heavy liquids and a Frantz magnetic separator. Approximately 100 zircon crystals were hand-picked from the remaining heavy, non-magnetic fraction, providing a range of grain size, morphology, transparency, alteration and occurrence of inclusions or cracks. The crystals were mounted into epoxy (Araldite) and the zircon mounts polished to about half thickness to expose the crystal interiors. The polished surfaces were imaged in back-scattered electron (BSE) and cathodoluminescence (CL) mode using a Philips XL30CP Scanning Electron Microscope (SEM) at the University of Edinburgh to identify internal zoning features, inherited material, inclusions and cracks. Suitable crystals for in-situ oxygen isotope analysis were selected using this information.

### 4.3. Hf isotope analysis

Hafnium isotope analysis was carried out at the NERC Isotope Geosciences Laboratory (NIGL) in Nottingham, using a Nu Instruments Nu-Plasma HR multi-collector ICP-MS coupled to a New Wave Research UP193SS 193nm solid state laser ablation system. For an improved wash-out a low volume ablation cell (NIGL zircon cell) was employed. Ablation was conducted in a He atmosphere (0.8-1.0 l/min). Ar make-up gas was sourced from a Nu Instruments DSN-100 desolvating nebuliser whilst aspirating 2 % HNO<sub>3</sub> and 0.1 molar HF to maintain constant plasma conditions.

At the time of analysis the mass spectrometer was fitted with a specially designed U-Pb collector block, which limits the number of Faraday cups available for Hf isotope analysis to seven. The instrument is therefore restricted to measuring <sup>173</sup>Yb, <sup>174</sup>Lu, <sup>175</sup>Lu, <sup>176</sup>(Yb, Lu, Hf), <sup>177</sup>Hf, <sup>178</sup>Hf and <sup>179</sup>Hf. The stable isotopes <sup>180</sup>Hf and <sup>181</sup>Hf are not analysed and emphasis is placed on the <sup>178</sup>Hf/<sup>177</sup>Hf stable isotope ratio for monitoring of data quality. A peak jumping routine including <sup>172</sup>Yb, to allow assessment of the effect of using a Yb mass bias correction for the Yb interference correction rather than the Hf mass bias correction, has been investigated but was found unnecessary with the data for both being equivalent within the increased uncertainty reflected by the low Yb concentrations.

The isobaric interference correction for <sup>176</sup>Yb was determined prior to each analytical session using Yb doped JMC475 Hf standards. This correction was determined for total Yb/Hf ratios of up to 0.3. These data were used to calculate a ratio for the <sup>176</sup>Yb/<sup>173</sup>Yb ratio of 0.79488. The Lu interference correction used the accepted ratio of <sup>176</sup>Lu/<sup>175</sup>Lu = 0.02653. During measurement the <sup>173</sup>Yb and <sup>175</sup>Lu peaks were monitored and corrections applied according to these ratios. Each day spiked and unspiked solution standards were analysed to monitor instrument performance and effectiveness of the corrections.

Ablation data were acquired using a static spot ablation protocol, a 50 µm beam and a 5-10 Hz laser pulse repetition rate. A fluence of 4-6 J/cm<sup>2</sup> and ablation time of 70 seconds resulted in an ablation rate of 0.05-0.09 µm/pulse (0.5-0.9 µm/sec). Total Hf signals varied between 4.5-6.5 V resulting in reproducibilities of the Mud Tank



reference material between 0.7 and 1.0  $\epsilon\text{Hf}$  units ( $2\sigma$ ). The Mud Tank zircon reference material was used to normalise the sample zircons and assess the reproducibility of all ratios. This included normalisation of the Lu-Hf ratio required for age correction. All values for Mud Tank were taken from Woodhead and Hergt (2005). All uncertainty components, including those for age and normalisation, were factored into the expanded uncertainty quoted.

For Hf isotope analysis zircons were selected for which U-Pb and (in most cases) oxygen isotope data already existed in order to enable correlation of the different data sets. Where possible multiple analyses were made on a single crystal. However, due to the much larger spot size of the laser in comparison to the ion probe this was seldom possible. Most data were obtained from crystal cores, which were easier to analyse as they often define the largest part of the crystal, and only rarely of the rim. Cracks and inclusions were always avoided and all analyses were carried out on the already existing SIMS spots or at least within the same CL growth zone. The ablation data were normalised to Mud Tank ( $^{176}\text{Hf}/^{177}\text{Hf}_{\text{solution}} = 0.282507 \pm 6$  and  $^{176}\text{Lu}/^{177}\text{Hf}_{\text{solution}} = 0.000042$  (Woodhead and Hergt, 2005)). Reproducibility of the Mud Tank standard was propagated into the uncertainty of the sample analysis.

In the rare cases where the laser drilled through the zircon grains or from an older inherited core into the surrounding magmatic rim, the analyses were examined using NIGL's time-resolved software, which allowed identification of the most stable parts of the profile and of distinguishable Hf isotope zones.

$\epsilon\text{Hf}$  values were calculated using a  $^{176}\text{Lu}$  decay constant of  $1.865 \times 10^{-11}\text{y}^{-1}$  (Scherer et al., 2001), the present-day chondritic  $^{176}\text{Lu}/^{177}\text{Hf}$  value of 0.0332 and  $^{176}\text{Hf}/^{177}\text{Hf}$  ratio of 0.282772 (Blichert-Toft and Albarède, 1997). To calculate two-stage Hf model ages the  $^{176}\text{Lu}/^{177}\text{Hf}$  ratios of the average crust ( $\text{TDM}_\text{C}$ ) ( $^{176}\text{Lu}/^{177}\text{Hf} = 0.015$  (Griffin et al., 2002)) and of the depleted mantle ( $^{176}\text{Lu}/^{177}\text{Hf} = 0.0384$  (Griffin et al., 2000)), the initial  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios of the zircon and the depleted mantle (present-day  $^{176}\text{Hf}/^{177}\text{Hf}$  ratio of the depleted mantle = 0.28325 (Nowell et al., 1998)), and the U-Pb SIMS age were used. For comparison, two-stage Hf model ages were also calculated based on the whole-rock  $^{176}\text{Lu}/^{177}\text{Hf}$  ratio of each sample ( $\text{TDM}_\text{W}$ ). A summary of the data can be found in Table 1, the full data set in Appendices 3a and 3b.

**Table 1**  
**Summary of oxygen and Hf isotope of zircons from the Lochnagar and Eltve plutons**

Sample	Age [Ma]	1SD [Ma]	$\delta^{18}\text{O}$ [‰]	$^{176}\text{Lu}/^{177}\text{Hf}$ (WR)	$^{176}\text{Lu}/^{177}\text{Hf}$	$^{176}\text{Lu}/^{177}\text{Hf}$	$^{176}\text{Lu}/^{177}\text{Hf}$ (Initial)	$\epsilon\text{Hf}$	95% TDMC con. [Ma]	95% TDMW con. [Ma]	95% n con.
<b>Lochnagar</b>											
AD1	419	4	7.0 (6.4-7.8)	0.008	0.282500 (0.282384-0.282614)	0.00114 (0.00055-0.00114)	0.282491 (0.282376-0.282606)	-0.7 (+3.4 to -4.8)	1.0 1459 (1198-1715)	60 1221 (1020-1419)	45 12
CrG	418	6	5.9 (5.5-6.4)	0.007	0.282553 (0.282495-0.282594)	0.00080 (0.00031-0.00205)	0.282546 (0.282492-0.282577)	1.2 (+2.3 to -0.7)	1.0 1334 (1264-1455)	61 1102 (1050-1193)	45 12
L1-03	420	3	6.6 (6.9-7.1)	0.007	0.282436 (0.282355-0.282473)	0.00065 (0.00031-0.00118)	0.282431 (0.282347-0.282469)	-2.8 (-1.5 to -3.8)	0.9 1592 (1507-1779)	56 1296 (1232-1436)	41 14
L1-06	420	4	6.4 (5.9-6.8)	0.004	0.282520 (0.282452-0.282562)	0.00185 (0.00092-0.00247)	0.282506 (0.282445-0.282545)	1.4 (+1.2 to -2.3)	1.3 1424 (1335-1560)	78 1105 (1044-1198)	52 5
L2-04	424	6	6.6	0.006	0.282484	0.00147	0.282483	-0.9	1.6 1473	95 1184	67 1
L2-12	419	4	6.3 (6.2-7.1)	0.004	0.282531 (0.282520-0.282548)	0.00154 (0.00127-0.00185)	0.282519 (0.282510-0.282534)	0.3 (+0.8 to -0.1)	0.9 1394 (1362-1415)	57 1084 (1062-1099)	38 6
L2-15	422	3	6.7 (6.0-7.5)	0.006	0.282521 (0.282435-0.282591)	0.00063 (0.00025-0.00187)	0.282515 (0.282430-0.282585)	0.2 (+2.7 to -2.8)	1.4 1403 (1245-1593)	86 1132 (1017-1270)	62 8
L3	423	5	6.6 (5.6-8.1)	0.004	0.282527 (0.282488-0.282583)	0.00107 (0.00055-0.00141)	0.282518 (0.282478-0.282518)	0.3 (+2.3 to -1.1)	0.9 1394 (1267-1484)	55 1086 (998-1147)	36 10
<b>Inherited zircons</b>											
L2-04_15_28	1046	15	6.5	0.006	0.282147	0.00049	0.282138	0.7	1.0 1855	50 1632	32 1
L2-04_15_29	1046	15	6.0	0.006	0.282157	0.00042	0.282149	1.1	1.1 1829	59 1613	38 1
L2-15_29a	1149	8	5.5	0.006	0.282355	0.00097	0.282334	10.0	1.5 1341	89 1288	62 1
L2-15_35b	1149	8	6.3	0.006	0.282198	0.00027	0.282192	4.9	1.3 1664	74 1521	51 1
L2-15_36a	1235	19	5.2	0.006	0.281760	0.00078	0.281742	-9.1	1.5 2622	82 2240	54 1
L2-15_32a	1235	19	5.7	0.006	0.282173	0.00048	0.282162	5.8	1.7 1676	95 1554	64 1
<b>Eltve</b>											
MO	423	3	6.4 (5.6-6.9)	0.005	0.282390 (0.282354-0.282432)	0.00061 (0.00034-0.00099)	0.282386 (0.282349-0.282425)	-4.4 (-3.0 to -5.7)	1.0 1692 (1605-1773)	62 1315 (1253-1372)	43 12
Cr-11	421	9	7.1 (6.4-7.9)	0.009	0.282339 (0.282315-0.282390)	0.00089 (0.00039-0.00146)	0.282332 (0.282305-0.282361)	-6.3 (-5.3 to -7.3)	0.8 1814 (1749-1872)	44 1532 (1481-1579)	34 13
Cr-17	414	6	6.6 (4.7-7.5)	0.009	0.282353 (0.282331-0.282390)	0.00051 (0.00034-0.00092)	0.282349 (0.282328-0.282386)	-5.9 (-4.6 to -6.6)	0.9 1778 (1697-1827)	50 1500 (1437-1541)	39 11
Cr-26	413	5	6.5 (5.3-7.6)	0.009	0.282356 (0.282324-0.282379)	0.00072 (0.00036-0.00116)	0.282350 (0.282316-0.282374)	-5.8 (-5.0 to -7.1)	1.0 1777 (1724-1853)	60 1501 (1459-1562)	46 11
Cr-15	413	5	6.2 (5.3-6.9)	0.009	0.282378 (0.282333-0.282413)	0.00077 (0.00049-0.00077)	0.282372 (0.282339-0.282406)	-5.1 (-3.8 to -6.6)	1.0 1728 (1647-1823)	62 1462 (1397-1539)	49 8
Si-01	412	6	7.1 (6.9-7.2)	0.008	0.282261 (0.282275-0.282290)	0.00092 (0.00039-0.00138)	0.282274 (0.282265-0.282283)	-8.6 (-6.3 to -9.9)	0.8 1947 (1928-1966)	46 1697 (1583-1614)	34 3
Q-23	408	6	7.0 (6.5-7.4)	0.008	0.282286 (0.282229-0.282293)	0.00077 (0.00051-0.00129)	0.282260 (0.282219-0.282284)	-9.2 (-8.3 to -10.6)	0.8 1981 (1928-2071)	44 1623 (1582-1693)	33 10
Q-25	408	4	6.2 (5.5-6.7)	0.007	0.282361 (0.282330-0.282385)	0.00064 (0.00035-0.00134)	0.282354 (0.282344-0.282382)	-5.8 (-4.8 to -6.9)	1.1 1770 (1710-1839)	68 1427 (1381-1478)	50 8
	405	12	6.0 (4.9-6.9)	0.007	0.282417 (0.282331-0.282565)	0.00128 (0.00076-0.00167)	0.282407 (0.282330-0.282553)	-4.0 (+1.1 to -7.1)	1.5 1655 (1328-1848)	83 1339 (1094-1484)	59 7
<b>Inherited zircons</b>											
Cr-15_4a	1036	22	7.0	0.009	0.282256	0.00039	0.282249	4.4	1.3 1611	73 1494	50 1
Cr-15_8a	1646	6	5.9	0.009	0.281749	0.00053	0.281733	-0.1	1.0 2374	75 2227	48 1

## 5. Results

### 5.1. Hf isotope data

#### 5.1.1 Lochnagar

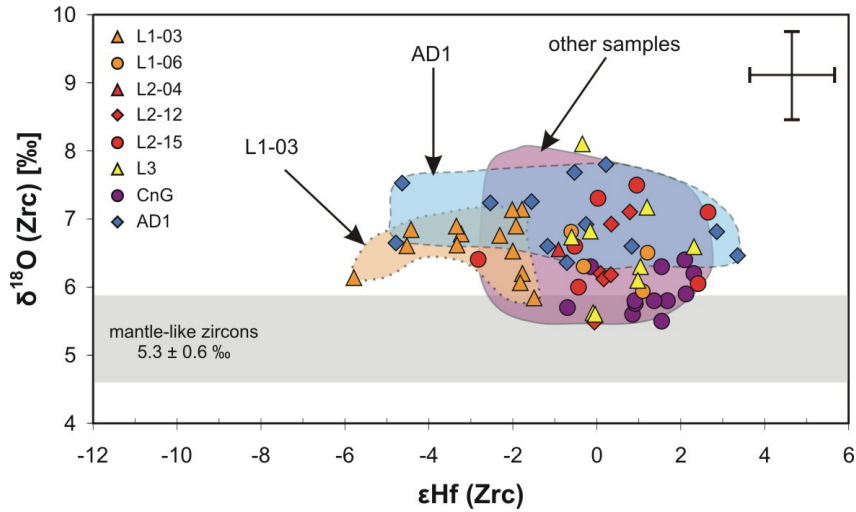


Fig. 4:  $\epsilon\text{Hf}$  vs.  $\delta^{18}\text{O}$  of zircons from the Lochnagar pluton ( $2\sigma$  error:  $\pm 1.0$   $\epsilon\text{Hf}$ ,  $\pm 0.6$  ‰). The majority of samples plot in the purple shaded area; samples L1-03 and AD1 are clearly different. L1-03 may comprise a different source, whereas AD1 may represent a mixture of at least two sources. Also note the difference in  $\epsilon\text{Hf}$  between L1-03 and L1-06, which were both collected within the same mapped unit.

Initial zircon  $\epsilon\text{Hf}$  values span 9.2  $\epsilon\text{Hf}$  units and range from +3.4 to  $-5.8 \pm 1.0$  ( $2\sigma$ ) (Fig. 4, Table 1). Resulting  $\text{TDM}_\text{C}$  Hf model ages vary between  $1198 \pm 65$  Ma and  $1779 \pm 60$  Ma (Table 1). The majority of samples (granite samples L1-06, L2-04, L2-12, L2-15, L3 and diorite sample CnG) have similar Hf isotope compositions and form a cluster between +2.7 and -2.8  $\epsilon\text{Hf}$  (Fig. 4). However, zircons of granite sample L1-03 and diorite sample AD1 are distinctly different. Zircons of L1-03 show only negative  $\epsilon\text{Hf}$  values and form a cluster at -1.5 to -5.8. L1-03 hence has a different composition than zircons of L1-06 (+1.2 to -2.3) even though both samples were collected from the same mapped granite facies. Zircons of diorite AD1 also extend to much more negative values, but overall form a very heterogeneous population ( $\epsilon\text{Hf} = +3.4$  to -4.8; =8.2  $\epsilon\text{Hf}$  units), which spreads over nearly the entire

range of values detected in zircons of the Lochnagar pluton (Fig. 4). This spread results from differences in  $\epsilon\text{Hf}$  between individual zircons; where multiple analyses were made on a single crystal  $\epsilon\text{Hf}$  values are always within error, and thus not resolvable (Fig. 5a-d). Therefore, in contrast to the results from  $\delta^{18}\text{O}$  data, resolvable variations occur between granite facies, between samples of the same facies and between zircon crystals of a single sample, but not within individual grains.

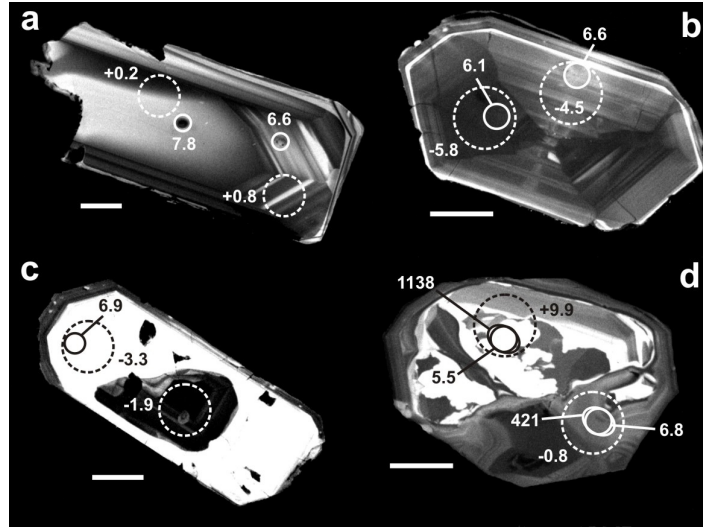


Fig. 5: Representative zircons with Hf isotope data (scale bar = 50  $\mu\text{m}$ , dashed circles:  $\epsilon\text{Hf} \pm 1.0$  ( $2\sigma$ ), circles:  $\delta^{18}\text{O} \pm 0.4\text{-}0.6$  ‰, ellipses: U-Pb  $\pm 1$  %).

a-c) Resolvable variation occurs between, but not within individual magmatic crystals (AD1 grain 10, L1-03 grain 16, L1-03 grain 23).  
a) Unzoned inner core domain and outer oscillatory zoned domain show resolvable variation in  $\delta^{18}\text{O}$ , but not in  $\epsilon\text{Hf}$  (L1-03, grain 16).  
d) Inherited grain with large xenocrystic core and magmatic rim. Core and rim display large variation (L2-15, grain 29).

Six analyses were carried out on older inherited zircons found in L2-04 ( $n=2$ ) and L2-15 ( $n=4$ ) (Table 1). One inherited zircon in L2-04 (U-Pb age =  $1046 \pm 33$  Ma) shows initial  $\epsilon\text{Hf}$  values of  $+1.1$  to  $+0.7 \pm 1.0$  and  $\text{TDM}_\text{C}$  model ages of  $1829 \pm 59$  Ma to  $1855 \pm 50$  Ma; at 424 Ma  $\epsilon\text{Hf}$  values were  $-12.5$  to  $-12.9 \pm 0.8$ . Three inherited cores in L2-15 with  $^{207}\text{Pb}/^{206}\text{Pb}$  ages between  $1149 \pm 8$  Ma and  $1235 \pm 19$  Ma have positive initial  $\epsilon\text{Hf}$  values of  $+10.0_{(1149 \text{ Ma})}$ ,  $+5.8_{(1235 \text{ Ma})}$  and  $+4.9_{(1149 \text{ Ma})} \pm 1.5$ , and corresponding  $\text{TDM}_\text{C}$  ages of  $1341 \pm 89$  Ma,  $1676 \pm 95$  Ma and  $1664 \pm 74$  Ma. At 422 Ma  $\epsilon\text{Hf}$  values ranged from  $-5.7$  to  $-12.1 \pm 1.3$ . A fourth inherited core has the

same U-Pb age ( $1149 \pm 8$  Ma), but a very different initial  $\epsilon\text{Hf}$  value of  $-9.1 \pm 1.5$  and  $\text{TDM}_\text{C}$  model age of  $2622 \pm 82$  Ma. At 422 Ma it had an  $\epsilon\text{Hf}$  value of  $-26.8 \pm 1.1$ .

### 5.1.2. Etive

Zircons from the Etive pluton range in initial  $\epsilon\text{Hf}$  from  $-3.0$  to  $-10.6 \pm 1.0$  ( $=7.6$  units) (Fig. 6) and show  $\text{TDM}_\text{C}$  model ages of  $1605 \pm 69$  Ma to  $2071 \pm 45$  Ma (Table 1). One outlier found in sample Q-25 of the Quarry Intrusion has an  $\epsilon\text{Hf}$  value of  $+1.1 \pm 1.7$  and a  $\text{TDM}_\text{C}$  of  $1328 \pm 97$  Ma.

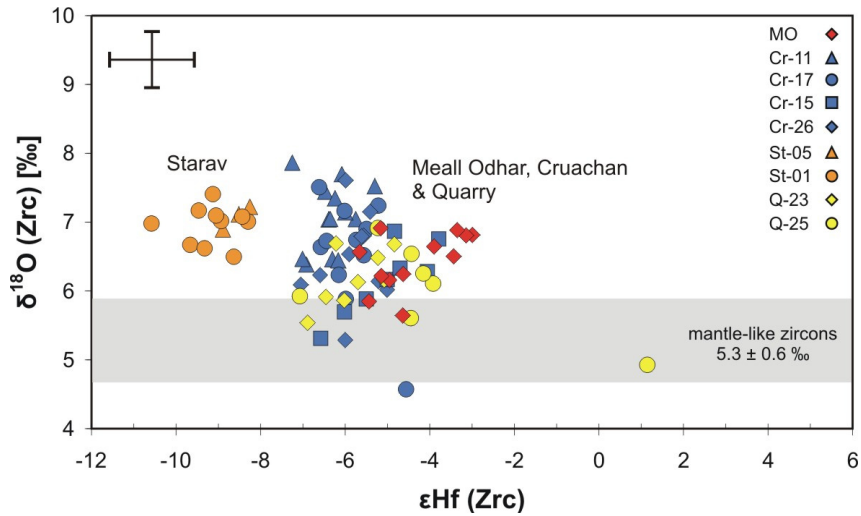


Fig. 6:  $\epsilon\text{Hf}$  vs.  $\delta^{18}\text{O}$  of zircons from the Etive pluton (error:  $\pm 1.0$   $\epsilon\text{Hf}$ ,  $\pm 0.4$  ‰ ( $2\sigma$ )).

The range in  $\epsilon\text{Hf}$  of  $7.6 \pm 1.0$  units is well outside the analytical uncertainty and similar to the spread found amongst zircons of the Lochnagar pluton ( $9.2 \pm 1.0$  units). However, in the Etive pluton this spread is defined by two distinct clusters of homogeneous samples, which both display negative  $\epsilon\text{Hf}$  values (Fig. 6). One cluster, which consists of zircons representing the Meall Odhar, Cruachan and Quarry Intrusions, has  $\epsilon\text{Hf}$  values of  $-3.0$  to  $-7.3 \pm 1.0$  and  $\text{TDM}_\text{C}$  ages of  $1605 \pm 69$  Ma to  $1872 \pm 43$  Ma. Of these samples zircons of the Meall Odhar Intrusion have the least negative  $\epsilon\text{Hf}$  values ( $-3.0$  to  $-5.7 \pm 1.0$ ) and those of Cruachan Intrusion sample Cr-11 the most negative ( $-5.3$  and  $-7.3 \pm 0.8$ ). The second cluster represents zircons from the Starav Intrusion (St-05 and St-01), which display more negative  $\epsilon\text{Hf}$  values

of  $-8.3$  to  $-10.6 \pm 0.8$  and older model ages of  $1928 \pm 52$  Ma to  $2071 \pm 45$  Ma ( $\text{TDM}_C$ ).

Two  $\epsilon\text{Hf}$  values were obtained from older inherited zircons found within Cr-15 (Table 1). They were dated using U-Pb zircon SIMS analysis at  $1036 \pm 22$  Ma and  $1646 \pm 6$  Ma (Paper 2). Their initial  $\epsilon\text{Hf}$  values are  $+4.4 \pm 1.3$  and  $-0.1 \pm 1.0$ , corresponding  $\text{TDM}_C$  ages are  $1611 \pm 73$  Ma and  $2374 \pm 75$  Ma respectively; at 413 Ma their  $\epsilon\text{Hf}$  values were  $-9.3 \pm 0.9$  and  $-27.2 \pm 0.9$ .

## 6. Discussion

### 6.1. Crustal growth vs. crustal recycling

The origin of the late Caledonian I-type granites and the reasons for the compositional differences between the granite suites have been the focus of numerous whole-rock studies. It has been proposed that the I-type granites represent the products of mixing between at least two different sources. However, whether these are mixtures of mantle (depleted and/or enriched) and infracrustal components (Clayburn et al., 1983; Halliday, 1984; Halliday et al., 1979, 1980; Harmon and Halliday, 1980) or of infracrustal and supracrustal components (possibly plus a mantle component) (Frost and O’Nions 1985) is unclear. Thus, it is uncertain whether the late Caledonian I-type magmatism may have played an important role in crustal growth. New in-situ zircon oxygen isotope data for the Lochnagar and Etive plutons (Paper 2) show that both plutons contain at most a small pristine mantle component, and were either derived from a mixture of mantle-derived and crustal sources or entirely from the crust since very few zircons have mantle-like  $\delta^{18}\text{O}$  values of  $5.3 \pm 0.6$  ‰ (Valley et al., 1998). Simple two-component magma mixing modelling based on zircon  $\delta^{18}\text{O}$  indicates that a contribution of up to 30 % by a supracrustal source such as the Dalradian metasedimentary country rocks may explain the range of  $\delta^{18}\text{O}$  values found in the plutons (Fig. 7). However, based on the lack of field evidence (e.g. xenoliths - pristine or partly digested - are very rare) (Frost and O’Nions, 1985) and the complexity observed in the plutons’ zircon

oxygen isotope data observed we envisage a more complex mixing/assimilation scenario involving more than two sources. From oxygen isotope data alone it is not possible to identify these sources, hence at present three questions remain unresolved:

(1) Does the proposed low  $\delta^{18}\text{O}$  mantle component represent contemporary mantle (c. 420 Ma) or melting of an ancient mafic lower crust source (e.g. mafic underplate), and therefore did the Caledonian I-granites involve any crustal growth?

(2) Which other crustal sources contributed to the Lochnagar and Etive plutons?

(3) What is the explanation for the observed whole-rock geochemical differences between the plutons? Zircon oxygen isotope compositions of the Lochnagar and Etive plutons are very similar, and therefore do not explain the observed whole-rock differences between the plutons, and on a wider scale between the Cairngorm and Argyll suites. This is not surprising considering that published whole-rock oxygen isotope data of the Lewisian Complex, Rhinns Complex, and Grenvillian basement, thus of rocks that may underlie the Grampian terrane, have very similar whole-rock  $\delta^{18}\text{O}$  values (Frost and O’Nions, 1985; Muir et al., 1994; Restrepo-Pace et al., 1997) (Fig. 7). Therefore the whole-rock differences are probably related to compositional variations amongst the lower crustal (or mantle) sources rather than being the result of varying degrees of crustal and mantle contribution.

In contrast to the zircon oxygen isotope data, the in-situ Hf isotope data of the plutons reveal large differences in  $\varepsilon\text{Hf}$  between the plutons, potentially providing an explanation for their whole-rock differences. Zircons from the Etive pluton have negative  $\varepsilon\text{Hf}$  values between -3.0 and  $-10.6 \pm 1.0$  ( $2\sigma$ ) with the exception of one outlier (grain 10 in Q-25:  $\varepsilon\text{Hf} = +1.1 \pm 1.7$ ), whereas zircons from the Lochnagar pluton display positive as well as negative  $\varepsilon\text{Hf}$  values between  $+3.4$  and  $-5.8 \pm 1.0$  ( $2\sigma$ ). Positive  $\varepsilon\text{Hf}$  values are generally interpreted as evidence for a mantle origin, whereas negative values reflect melting of ancient crust (e.g. Amelin et al., 1999; Vervoort et al., 2000). Based on this the Etive pluton is predominantly derived from a crustal source and does not contain a ~420 Ma mantle component, whereas the Lochnagar pluton appears to be the product of melts derived from the mantle and from a crustal source. However, in both plutons a contribution by contemporary depleted mantle can be precluded on the base of  $\varepsilon\text{Hf}$  data, which show that even the

most positive  $\epsilon_{\text{Hf}}$  value in Lochnagar (i.e.  $+3.4 \pm 1.1$ ) indicates a strong crustal affinity in comparison to the  $\sim 420$  Ma depleted mantle ( $+16 \pm 3$  (Vervoort and Blichert-Toft, 1999) (range of  $\pm 3$   $\epsilon_{\text{Hf}}$  units represents the range observed in present-day MORB (Griffin et al., 2000)). Further evidence is provided by calculated Hf model ages, which are considerably older than the zircon U-Pb crystallisation ages (Lochnagar: U-Pb = 424-413 Ma,  $\text{TDM}_{\text{C}} \sim 1.7$ -1.1 Ga,  $\text{TDM}_{\text{W}} \sim 1.4$ -1.0 Ga; Etive: U-Pb = 423-407 Ma,  $\text{TDM}_{\text{C}} \sim 2.1$ -1.3 Ga,  $\text{TDM}_{\text{W}} \sim 1.8$ -1.2 Ga) (Fig. 8 & 9). However, enriched mantle typically has  $\epsilon_{\text{Hf}}$  values closer to CHUR ( $\epsilon_{\text{Hf}} = 0$ ).

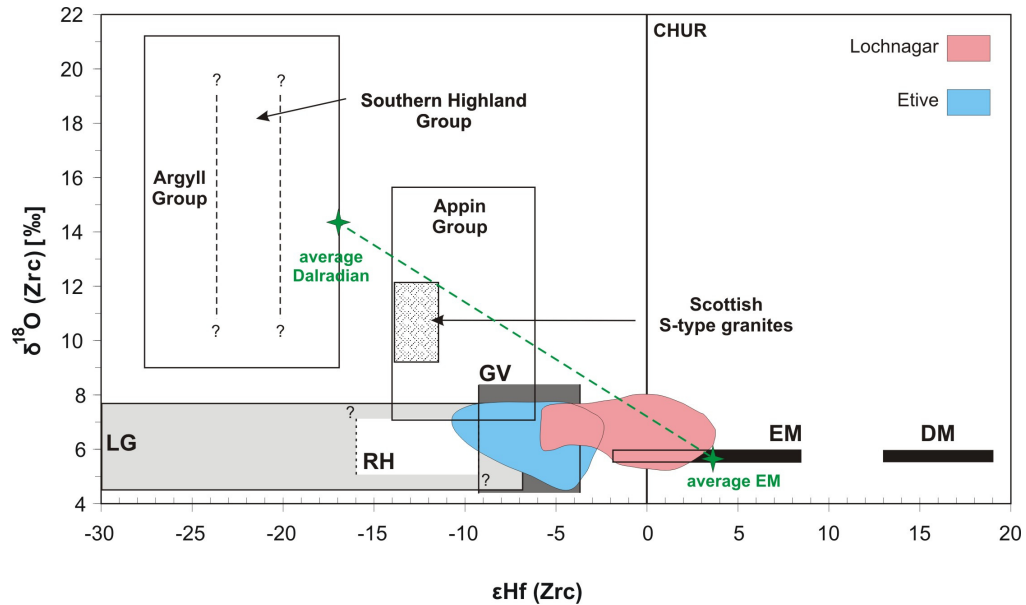


Fig. 7:  $\epsilon_{\text{Hf}}$  vs.  $\delta^{18}\text{O}$  of zircons from the Lochnagar and Etive plutons showing the relationship to their potential supracrustal and infracrustal sources. Zircons from both plutons show no overlap with the field defined by depleted mantle (DM, re-calculated at 420 Ma), but those from the Lochnagar pluton show strong overlap with enriched mantle (EM). The mixing line (green dashed line) reflects simple two-component mixing between EM and average Dalradian (i.e. Appin, Argyll and Southern Highland groups). Based on this mixing modelling both plutons may contain up to 30 % Dalradian material. However, the complexity and variation observed in the zircon oxygen isotope data indicates involvement of more than two sources. Large overlap exists with fields representing the plutons' potential lower crustal source rocks (i.e. Lewisian granulites = LG, Rhinns Complex = RH, Grenville-age basement = GV). Hf isotope data (at 420 Ma) of potential sources were calculated based on published Nd isotope data (assuming a Hf-Nd correlation of the terrestrial array (Vervoort and Blichert-Toft, 1999)) by Anderson et al. (2004), Canning et al. (1998), Frost and O'Nions, (1985), Halliday (1984), Hamilton et al. (1980), Harmon (1983), Kay (1980), Muir et al. (1994), O'Nions et al. (1983), Restrepo-Pace et al. (1997), Thirlwall (1982).

Strong evidence exists from Nd isotope data that the mantle below Scotland is highly heterogeneous and contains depleted as well as enriched mantle domains.



Evidence for this was provided by Thirlwall (1982), who carried out a study on Scottish Old Red Sandstone lavas located to the north and south of the Highland Boundary Fault (HBF) and demonstrated that lavas to the south of the HBF display  $\epsilon\text{Nd}_{410 \text{ Ma}}$  values up to +6.4 (estimated  $\epsilon\text{Hf} = +11.7$  assuming a Hf-Nd correlation of the terrestrial array (Vervoort et al., 1999)), which indicates involvement of a depleted mantle source in their genesis. However, lavas to the north of the HBF, which may be representative of the mantle below the Lochnagar and Etive plutons, display  $\epsilon\text{Nd}$  values between +1.1 to -3.6 (estimated  $\epsilon\text{Hf} = +4.5$  to -1.9), which was interpreted as evidence for an enriched mantle domain. In addition, Canning et al. (1998) carried out Nd isotope analyses on two lamprophyre suites from northern and southern Scotland and found two distinct mantle domains separated by the Great Glen Fault. The northern domain ranged in  $\epsilon\text{Nd}_{400 \text{ Ma}}$  from -6.4 to -12.8 (estimated  $\epsilon\text{Hf} = -5.7$  to -14.4), and the southern domain from +3.9 to -3.4 (estimated  $\epsilon\text{Hf} = +8.3$  to -1.6). The  $\epsilon\text{Nd}$  data of the southern domain extends to more positive values, but is generally similar to the data reported by Thirlwall (1982) for lavas north of the HBF, and may therefore be a reasonable estimate of the mantle composition below the plutons. Thus, based on this data and our Hf isotope data a contribution by a contemporary enriched mantle source for the Lochnagar pluton cannot be ruled out and is consistent with the zircons with mantle-like  $\delta^{18}\text{O}$  values. As zircons from the Etive pluton display much more negative  $\epsilon\text{Hf}$  values than those of the Lochnagar pluton the contribution by c. 420 Ma enriched mantle was probably considerably smaller. Melting of an ancient mafic underplate to produce zircons with negative  $\epsilon\text{Hf}$  and mantle-like  $\delta^{18}\text{O}$  values may account for the mantle-like zircons observed in the Etive pluton.

By combining the new Hf and oxygen isotope data the questions of continental growth vs. crustal recycling may now be partially resolved. Neither the Lochnagar nor the Etive pluton contain a significant contemporary depleted mantle component; based on the number of zircons with mantle-like  $\delta^{18}\text{O}$  values and positive  $\epsilon\text{Hf}$  values a contribution by enriched mantle is likely for the Lochnagar pluton, but due to generally crustal  $\epsilon\text{Hf}$  values less so for the Etive pluton. Both plutons appear to contain a large crustal component, which probably represents a mixture of supra- and infracrustal sources. Thus, we conclude that at least for the Lochnagar pluton it

cannot be ruled out that it made a significant contribution to crustal growth. However, without more detailed information on the composition and ages of the mantle and crustal sources, which would permit us to carry out AFC modelling (DePaolo, 1981), the proportion of new crust cannot be accurately quantified.

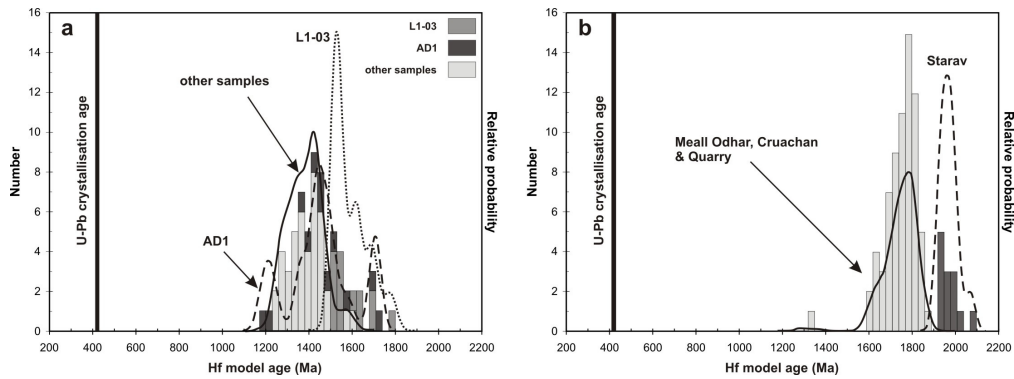


Fig. 8: Hf model ages ( $TDM_C$ ) of zircons from (a) the Lochnagar pluton and (b) the Etive pluton (probability curves were calculated at  $1\sigma$ , bin width =  $1\sigma$ ).

## 6.2. Lower crustal sources

$\epsilon_{Hf}$  values indicate that the whole-rock geochemical differences between the two plutons are partly the result of compositional variations between the mafic components involved, an enriched contemporary component in the Lochnagar pluton and an ancient mafic underplate in the Etive pluton. However, variations between their infracrustal sources will also be a controlling factor.

Several models have been proposed for the nature, age and affinity of the lower crust below the Grampian Highlands. These are based on geophysical constraints, geochemical and isotopic data for the late Caledonian granites, U-Pb ages of inherited zircons from the granites and wider geological arguments, since appropriate rocks are not exposed in this part of Scotland. U-Pb ages of inherited zircons cannot be considered clear evidence as their origin is ambiguous in the late Caledonian I-type granites. Detrital zircons from the Dalradian Supergroup, the country rocks hosting the granites, display the same ages as inherited zircons in the granites. Thus it is likely that the latter represent minor assimilation of Dalradian rather than lower crustal source material (Paper 2).

The *Lewisian Complex* crops out on the Outer Hebrides, on the coastal mainland of western Scotland, and as inliers within the Moine metasediments located to the east of the Moine Thrust (Park et al., 2002). Geophysical data indicate that these exposures form part of a broad area, which extends further to the north and west. The Lewisian Complex predominantly consists of granulite facies tonalitic gneisses (c. 70 %), which contain mafic and ultramafic enclaves and supracrustal metasediments (e.g. Park, 1991). Nd isotope data show that the gneisses are derived from an igneous protolith that separated from the mantle at c. 2.9 Ga (Muir et al., 1994).

The *Rhinns Complex* is exposed on the islands of Islay and Colonsay in the west of Scotland and on Inishtrahull in Ireland, but it is not clear how far this basement extends beneath the Grampian Highlands. Based on Nd isotope data from Caledonian I-type granites it has been proposed that it forms the basement onto which the Dalradian metasediments (at least in an area of c. 100 km x 600 km) south of the Great Glen Fault were deposited (Dickin and Bowes, 1991; Upton et al., 1998). However, no contacts between the Rhinns Complex and any younger metasedimentary strata can be found (Rollin, 1994). The Rhinns Complex comprises deformed syenites, gabbros and minor felsic and mafic intrusions that were derived from a juvenile mantle source at c. 1.8 Ga (Daly et al., 1991; Muir, 1990).

*Grenvillian basement* (c. 1.2-1.0 Ga) can be found in only a single location, i.e. in the Glenelg-Attadale Inlier in the northwest Highlands. The inlier contains two units; the Western Unit is believed to represent correlatives of the Lewisian Complex (Barber and May, 1975; May et al., 1993), but the Eastern Unit comprises eclogites, which formed and retrogressed during the Grenville orogeny (Brewer et al., 2003; Sanders et al., 1984) as constrained by zircon and titanite dating (Brewer et al., 2003).

Rocks of the *Dava and Glen Banchor successions*, i.e. gneissose and locally migmatitic psammite and semi-pelite with subordinate quartzite, are known to also underlie parts of the Dalradian Supergroup (Highton et al., 1999; Piasecki, 1980). Dating of detrital zircons has shown that at least rocks of the Dava Succession were predominantly derived from Palaeoproterozoic- and Grenville-age sedimentary protoliths (Highton et al., 1999).

Although these potential lower crustal source rocks are exposed in only relatively small areas and predominantly in the west of Scotland, U-Pb SHRIMP dating of detrital zircons from the Dalradian Supergroup (Cawood et al., 2003) has shown that Archaean- (2.8-2.7 Ga), Palaeoproterozoic- (1.8-1.5 Ga) and Grenville-age (1.1-0.9 Ga) crust must exist across a much larger area.

Two-stage Hf model ages are commonly used to constrain the crustal residence ages of granite protoliths. However, interpretations based on Hf model ages can be ambiguous for the following reasons:

(1) Lu and Hf fractionate during magmatic processes, which leads to significant differences in the  $^{176}\text{Lu}/^{177}\text{Hf}$  ratio between primitive and evolved rocks. For example, high Lu/Hf ratios, typical of mafic crust, will give maximum Hf model ages, whereas low Lu/Hf ratios representative of felsic crust will give minimum Hf model ages (Nebel et al., 2007). Unfortunately it is not possible to determine the  $^{176}\text{Lu}/^{177}\text{Hf}$  ratio of the protolith, and therefore calculations have to be based on approximate (assumed) values. Using the  $^{176}\text{Lu}/^{177}\text{Hf}$  ratio of the granite whole-rock should be the most logical choice as it should be representative of the protolith. However, this assumes that the magma did not undergo any Lu/Hf fractionation during its evolution. Alternatively the  $^{176}\text{Lu}/^{177}\text{Hf}$  of the average crust ( $^{176}\text{Lu}/^{177}\text{Hf} = 0.015$ ; Griffin et al., 2002), the average felsic lower crust ( $^{176}\text{Lu}/^{177}\text{Hf} = 0.0093$ ; Vervoort and Patchett, 1996) or the average mafic crust ( $^{176}\text{Lu}/^{177}\text{Hf} = 0.022$ ; Vervoort and Patchett, 1996) may be used, which is as large an assumption as using the first approach.

(2) In an environment where multiple sources were mixed, a likely scenario based on the large spread in zircon  $\delta^{18}\text{O}$  and  $\epsilon\text{Hf}$  data found in both plutons, the Hf model ages will reflect an intermediate age between the different end-members. Thus, only if a granite has a simple source, did not undergo any mixing and the correct  $^{176}\text{Lu}/^{177}\text{Hf}$  was used, will the Hf model ages reflect the true time of separation from the mantle.

In this study we calculated Hf model ages using the  $^{176}\text{Lu}/^{177}\text{Hf}$  of the average crust ( $\text{TDM}_\text{C}$ ), and for comparison also using the whole-rock  $^{176}\text{Lu}/^{177}\text{Hf}$  ratio of each granite sample ( $\text{TDM}_\text{W}$ ) (Fig. 9). The resulting model ages differ by ~150-300 m.y., with  $\text{TDM}_\text{C}$  ages representing the older ages. For Lochnagar,  $\text{TDM}_\text{C} \sim 1.8\text{-}1.2$

Ga and  $TDM_W \sim 1.4\text{-}1.0$  Ga; for Etive,  $TDM_C \sim 2.1\text{-}1.3$  Ga and  $TDM_W \sim 1.8\text{-}1.2$  Ga. Thus, linking the ages to any of the potential lower crustal sources is difficult. The best example to illustrate this is the Starav Intrusion of the Etive pluton, for which  $TDM_C$  ages range from 2.1 Ga to 1.9 Ga and  $TDM_W$  from 1.7 Ga to 1.6 Ga. Based on  $TDM_C$  ages the Starav Intrusion comprises magmas derived from melting of Rhinns and Lewisian lower crust, whereas based on  $TDM_W$  ages it is sourced in the Rhinns Complex and Grenville-age basement (1.2-1.0 Ga). Nevertheless,  $TDM_C$  and  $TDM_W$  Hf model ages provide strong evidence that the lower crust beneath the Etive pluton is, at least in parts, older than beneath the Lochnagar pluton.

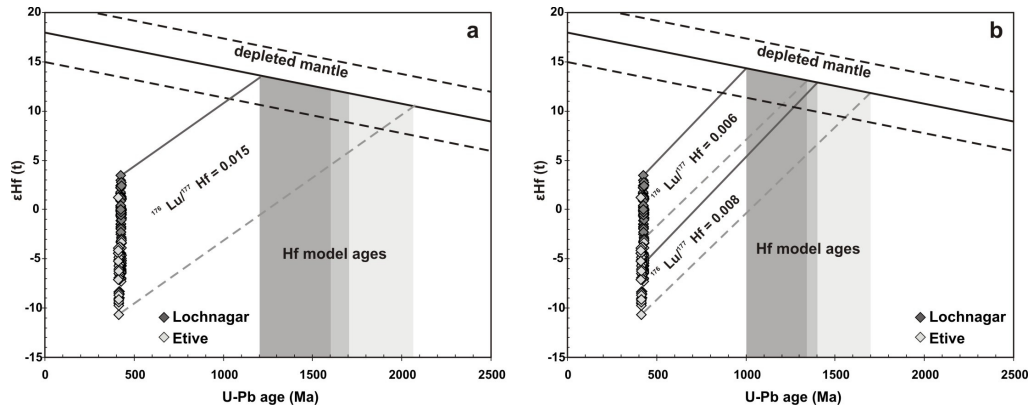


Fig. 9: Hf model ages of the Lochnagar and Etive plutons calculated based on (a) the  $^{176}\text{Lu}/^{177}\text{Hf}$  ratio of the average crust, and (b) the plutons' average whole-rock  $^{176}\text{Lu}/^{177}\text{Hf}$  ratios.

In general, the lower crust is known to be highly heterogeneous due to melting and intracrustal differentiation (Rudnick, 1995). Thus, the most likely model for the lower crust beneath the Lochnagar and Etive plutons is that it represents a complicated mixture of Archaean- to Neoproterozoic-age material. The proportional contributions from different sources varies between the plutons, with the Lochnagar pluton predominantly representing larger proportions of Mesoproterozoic-age lower crust, and the Etive pluton of Palaeo- and Mesoproterozoic-age lower crust. This is supported by the  $\epsilon\text{Hf}$  vs.  $\delta^{18}\text{O}$  diagram (Fig. 7), which for zircons from the Lochnagar pluton shows large overlap with the field for the Grenville basement, and for zircons from the Etive pluton with fields for the Lewisian granulites, Rhinns Complex and Grenville basement. Evidence for the involvement of several sources

can be found in both plutons. For Lochnagar this can be demonstrated in samples of the L1 granite and the Allt Darrarie diorite. Even though both L1 samples were collected within the same mapped unit, they have distinct Hf isotope compositions (L1-03: -1.5 to -5.8; L1-06: +1.2 to -2.3), which overlap by only 0.8  $\epsilon\text{Hf}$  units. This suggests that the L1 granite and therefore the Lochnagar pluton comprise at least two sources of differing Hf isotope compositions. All analysed samples except the Allt Darrarie diorite were predominantly derived from either one of those sources; zircons of the Allt Darrarie diorite, which display nearly the same range of  $\epsilon\text{Hf}$  values (8.2 units) as the entire pluton, appear to represent a mixture of both sources. Evidence of at least two sources was also discovered in the Etive pluton. Zircons of the Meall Odhar, Cruachan and Quarry intrusions were derived from a source with  $\epsilon\text{Hf}$  values between -3.0 and -7.3, whereas zircons of the Starav Intrusion form a separate cluster at -8.3 and -10.6. In contrast to the Lochnagar pluton, these sources do not appear to have mixed with each other. The observed Hf isotope heterogeneities between the plutons' mapped units, within units and between zircon crystals provide further evidence that magma generation most likely occurred in a deep crustal hot zone and pluton emplacement by incremental assembly as has been proposed by (Paper 1 & 2).

## 6. Conclusions

- 1)  $\epsilon\text{Hf}$  and Hf model ages indicate different sources for the Lochnagar and Etive plutons. Based on in-situ zircon oxygen isotope analysis both plutons comprise a mantle component. From  $\epsilon\text{Hf}$  values a major contemporary depleted mantle component ( $\epsilon\text{Hf}_{420 \text{ Ma}} = +16$ ) can be precluded. However, with  $\epsilon\text{Hf}$  values between +3.4 and  $-5.8 \pm 1.0$  ( $2\sigma$ ) an enriched mantle component cannot be excluded in the Lochnagar pluton. As zircons from the Etive pluton display more negative  $\epsilon\text{Hf}$  values between -3.0 and  $-10.6 \pm 1.0$  ( $2\sigma$ ) melting of an ancient mafic underplate is proposed. Without knowing the composition and ages of the plutons' potential mantle and crustal sources in more detail it is not possible to unambiguously quantify the proportion of new crust. For the Lochnagar pluton a

significant contribution to crustal growth cannot be precluded, however, this appears less likely for the Etive pluton.

- 2) Both plutons appear to comprise multiple sources. In the Lochnagar pluton one L1 granite sample melted older material than the other granite samples; evidence of mixing between the sources can be observed in the Allt Darrarie diorite. In the Etive pluton the Starav Intrusion melted much older lower crustal material than the Meall Odhar, Cruachan and Quarry intrusions. Evidence for mixing between these sources was not found in the Hf isotope data.
- 3) The Lochnagar and Etive plutons also show variations between their lower crustal sources. Hf model ages provide strong evidence that the Etive pluton has sourced much older lower crust than the Lochnagar pluton. However, due to the ambiguities of calculating Hf model ages, the potential sources (Lewisian Complex, Rhinns Complex and Grenvillian basement) cannot be easily or quantitatively linked to the plutons. Thus, the most likely model for the lower crust beneath the Lochnagar and Etive plutons is that it represents a complex mixture of remelted material of Archaean- to Neoproterozoic-age material. The contributions from these sources varies between the plutons, with the Lochnagar pluton predominantly representing larger proportions of Mesoproterozoic-age, and the Etive pluton of Palaeo- and Mesoproterozoic-age lower crust. If the two plutons are representative of the Argyll and Cairngorm suites, this study lends support to the hypothesis that the geochemical distinction between these suites lies dominantly in the differences in the ages and compositions of their underlying lower crustal and potentially their mantle sources.

**V.**

**PAPER 4**

**An integrated O, U-Pb and Hf isotope  
study of zircons in S-type granites**



# An integrated O, U-Pb and Hf isotope study of zircons in S-type granites

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## Abstract

In contrast to I-type granites, which are known to comprise multiple sources with complex petrogenetic histories, S-type granites are thought to typically form by melting of a single supracrustal/sedimentary source. However, this integrated oxygen, U-Pb and Hf isotope study of zircons from three Scottish Caledonian (~460 Ma) S-type granites (Kemnay, Cove and Nigg Bay) demonstrates that all three comprise two or more sources. This conflicts with field evidence, which has been interpreted to indicate that the granites were generated in-situ by melting their current country rocks. As zircons from the Kemnay and Cove granites show <sup>18</sup>O-enriched  $\delta^{18}\text{O}$  values of  $9.2 \pm 0.6 \text{ ‰}$  ( $2\sigma$ ) and  $10.0 \pm 0.6 \text{ ‰}$ , respectively they are likely to have sourced predominantly supracrustal material including their current host country rocks. By contrast, zircons from the Nigg Bay Granite have much lower  $\delta^{18}\text{O}$  values of  $7.3 \pm 0.6 \text{ ‰}$  suggesting mixing between a supracrustal source and a

## 1. Introduction

The distinction of I-type (igneous or infracrustal precursor) granites from S-type (sedimentary or supracrustal precursor) granites, based on extensive whole-rock geochemical studies of the Lachlan Fold Belt granites of southeastern Australia (Chappell and White 1974), implies that granites have distinct and recognisable sources that may be identified from their mineralogy and geochemistry. Subsequent studies have shown that granites have complicated petrogenetic histories and commonly comprise multiple sources (John and Wooden, 1990; Kemp et al., 2007; Kemp and Hawkesworth, 2003; Miller et al., 1990). More recent work in the Lachlan Fold Belt has demonstrated that I-type granites may contain 50 % - and S-types up to 10 % - of a component with a mantle-like signature (Collins, 1996, 1998; Gray, 1984), indicating mixing between crustal- and mantle-derived melts.

Traditionally, studies of granite petrogenesis have been based on whole-rock geochemical and isotopic data. These deliver averaged information and are sensitive to mineralogical modification and chemical exchange. Thus, whole-rock data often do not represent the magma composition from the time of crystallisation, and may lead to incorrect interpretations and models.

By exploiting recent advances in in-situ microanalysis we may address the question of granite sources using geochemical information stored in zircon, a common refractory accessory mineral in granitoid rocks that retains information about its host melt. As zircon typically represents an early-crystallising phase in silicic magmas, it records early-stage melt compositions, and in the form of growth zones, any subsequent changes in melt composition during zircon growth (Hoskin and Schaltegger, 2003; Shore and Fowler, 1996; Vavra, 1990, 1993, 1994). Since zircon contains significant concentrations of U and Th (ppm level) and Hf (percent level) (Kinny and Maas, 2003), it is suitable not only for oxygen isotope analysis but also for U-Pb and Hf isotope analysis. Due to the high spatial resolution of ion microprobes (SIMS) multiple analyses may be made in a single crystal, enabling detection of previously inaccessible intra-grain variations and correlation with textural information. In addition, as SIMS analysis is essentially non-destructive, oxygen and U-Pb isotope analyses may be made on the same c. 20  $\mu\text{m}$  spot, followed

by Hf isotope analysis by laser ablation (LA-MC-ICPMS) on a c. 50  $\mu\text{m}$  spot, allowing integration of the data sets. This approach may be used to constrain the emplacement ages of plutons (U-Pb data), the relative mantle and crustal contributions (O and Hf isotope data) and the crustal residence ages of their sources (Hf isotope data), thus providing a major advance in deciphering the sources and petrogenetic histories of granites. Studies applying this integrated zircon approach have already been carried out on zircons from the Lachlan Fold Belt (Kemp et al., 2007) and from the Scottish late Caledonian (c. 430-400 Ma) I-type granites (Paper 3). However, to our knowledge no such studies have to date been undertaken on zircons from S-type granites. In contrast to I-type granites, which have been shown to commonly represent a complex mixture of mantle-like, infra- and/or supracrustal components (e.g. Kemp et al., 2007), S-type granites commonly comprise only supracrustal/sedimentary source material(s) (e.g. Chappell and White, 1974). By studying zircons from S-type granites it may be possible to obtain essentially unmodified information about their supracrustal precursor, and therefore of one commonly inferred end-member component in I-type granites.

The Scottish late Caledonian I-type granites have been shown to contain a small proportion of older inherited zircons (e.g. Pidgeon and Aftalion, 1978; Paper 2). However, to date it has not been possible to resolve whether these were inherited from an infracrustal or supracrustal source (e.g. their Dalradian Supergroup country rocks). In order to characterise the supracrustal component we selected three representative Caledonian S-type granites (Kemnay, Cove and Nigg Bay), which are thought to have been generated more or less in-situ by melting of a supracrustal precursor, most likely within the Dalradian Supergroup. All three granites are currently hosted by the same country rocks (i.e. the Aberdeen Formation) and are petrographically and geochemically very similar, but differ greatly in size. The specific aims of this study were to use high-precision in-situ oxygen, U-Pb and Hf isotope data from zircons to constrain and compare the isotopic composition of their sources and their petrogenetic evolution, which may differ due to their different pluton sizes.

## 2. Geological background

### 2.1. The Caledonian S-type granites

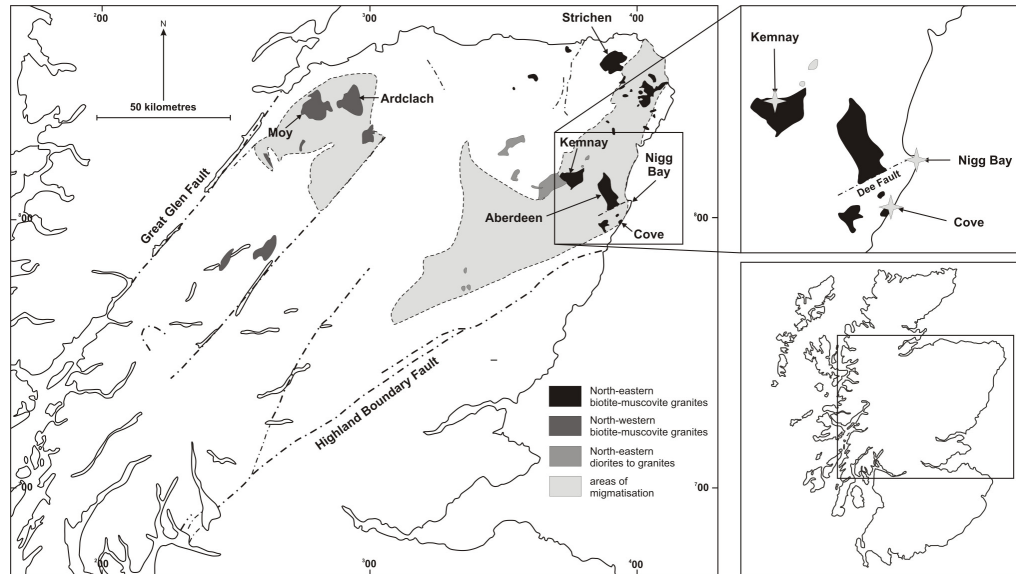


Fig. 1: Map showing the locations of the syn- and late-tectonic granites and diorites that intruded the Grampian Highlands, of the target plutons Kemnay, Cove and Nigg Bay and of collected samples (after Stephenson and Gould, 1995).

The Caledonian S-type granites of the Grampian Highlands of Scotland intrude the Dalradian Supergroup, a c. 25 km thick sequence of deformed and metamorphosed late Neoproterozoic to Lower Ordovician shallow- and deep-water sediments and volcanics (Harris et al., 1978, 1994; Stephenson and Gould, 1995). They were generated contemporaneously with and subsequent to the Grampian Event (c. 480 Ma and 465 Ma; Oliver, 2001), which resulted from the collision of the Laurentian continental margin with a volcanic arc that developed during closure of the Iapetus Ocean. The Grampian Event has been divided into four episodes of deformation (D1-D4) (Strachan et al., 2002). D1 defines the onset of deformation and created major folds, ductile shears, tectonic fabrics and greenschist-facies metamorphism. D2 (c. 470 Ma) represents the main phase of deformation and involved rotation and stacking of fold nappes, and Barrovian metamorphism. In the northeastern and possibly in the northwestern Grampian Highlands D2-induced regional metamorphism caused large-scale migmatisation (Fig. 1). Some migmatites

formed by diffusion of elements via a water-rich fluid phase, but the majority were produced by partial melting of the host rock (Munro, 1986). D3 caused localised lower to middle amphibolite-facies metamorphism and in-situ generation of granitic melts and pegmatites. D4 was the weakest deformational episode and created broad upright folds and brittle structures (Strachan et al., 2002). Following crustal thickening, the Grampian terrane experienced cooling, isostatic uplift and decompression in the later stages of the Grampian Event and subsequent to it (465 Ma to 435 Ma) (Dempster et al., 1995; Dewey and Mange, 1999; Oliver, 2001; Oliver et al., 2000; Soper et al., 1999).

The Grampian Event was accompanied by syn- and late-tectonic magmatism. The syn-tectonic mafic and ultramafic 'Newer Gabbros' are large, layered intrusions of cumulate peridotite, gabbro, norite and syenite (Read, 1961), for which Dempster et al. (2002) reported a zircon TIMS age of  $470 \pm 9$  Ma. The late-tectonic biotite-muscovite granites display peraluminous compositions, high initial  $^{87}\text{Sr}/^{86}\text{Sr}$  values ( $> 0.71$ ), and high proportions of Dalradian country rock xenoliths and older inherited zircons, all features typical of S-type granites (Harmon, 1983; Pankhurst, 1974; Pidgeon and Aftalion, 1978) (Fig. 1; Stephenson and Gould, 1995; Strachan et al., 2002). They predominantly occur in the previously migmatised areas in northeastern and northwestern Grampian Highlands where they were probably generated due to crustal thickening and radiogenic heating following arc-continent collision, and locally by intrusion of the 'Newer Gabbros' (Gould, 1997; Oliver, 2001).

The North-eastern biotite-muscovite granites, which formed between 475 Ma and 465 Ma (Kneller and Aftalion, 1987; Oliver, 2001; Pidgeon and Aftalion, 1978), range in size from small lensoid or sheet-like bodies (e.g. Nigg Bay Granite) to larger masses (e.g. Cove:  $\sim 1.7 \text{ km}^2$ , Kemnay:  $36 \text{ km}^2$ , Aberdeen:  $90 \text{ km}^2$ ). Gradational contacts with the surrounding migmatitic Dalradian country rocks and the occurrence of partly or fully digested and modified metasedimentary xenoliths led to the interpretation that the granites were generated more or less in-situ. However, as many granites show magmatic foliations, sharp contacts with their country rocks, and contain country rock xenoliths with sharp, angular boundaries it has been suggested

that while partial melting of their current country rocks has played an important part, many granites may have been generated at deeper levels (Munro, 1986).

The North-western biotite-muscovite granites comprise variably foliated and recrystallised granites and granodiorites with subordinate leucogranites and pegmatites. Only two U-Pb ages exist for these granites -  $455 \pm 27/-15$  Ma (monazite) for the Moy Granite (Zaleski, 1983) and  $475 \pm 7$  Ma (monazite) for the Ardclach Granite (Zaleski, 1983). The North-western biotite-muscovite granites were interpreted to have formed towards the end of the Grampian orogenic activity, possibly during decompression following isostatic uplift (Oliver, 2001; Stephens, 1988).

## *2.2. The Kemnay, Cove and Nigg Bay granites*

The Kemnay, Cove and Nigg Bay granites are located close to Aberdeen in the northeastern Grampian Highlands where they crop out over areas of c.  $36 \text{ km}^2$ ,  $1.7 \text{ km}^2$  and less than  $1 \text{ km}^2$ , respectively, in migmatised rocks of the Aberdeen Formation (Fig. 1). Early studies considered the Aberdeen Formation, which comprises psammites, semi-pelites and subsidiary pelites with sparse calc-silicate ribs, to be part of the Argyll Group of the Dalradian Supergroup (Munro, 1986); however, evidence has been found that at least the area south of the river Dee is stratigraphically equivalent to the lower units of the Southern Highland Group (Gould, 1997; Stephenson and Gould, 1995).

### *2.2.1. The Kemnay Granite*

The Kemnay Granite forms a c.  $36 \text{ km}^2$  large body around Kemnay and Kintore. It comprises a dominant homogeneous central part and a c. 500 m wide gradational contact zone, which grades into the surrounding migmatitic semi-pelites and feldspathic psammites. In the contact zone the granite is heterogeneous, and shows diffuse compositional layering and abundant partially digested migmatitic country rocks (Gould, 1997).

The central part of the Kemnay Granite consists of medium-grained (1.5-2.5 mm), white biotite-muscovite granite, which displays a weak magmatic foliation

defined by biotite and to a lesser extent by feldspar. It occasionally contains biotite-rich schlieren that are typically 5-10 cm wide and 10 cm long. Some areas show evidence of recrystallisation, hydrothermal alteration and a later tectonic fabric (Gould, 1997).

The inequigranular to weakly porphyritic granite comprises phenocrysts of plagioclase (up to 7.5 mm), quartz (up to 5mm, but recrystallised to smaller crystals of 1.5 mm), K-feldspar (up to 5 mm), and less commonly, biotite (up to 5 mm), and a matrix (1.5-2.5 mm) of the same minerals. Plagioclase (c. 35 %) is typically strongly altered to sericite and in parts replaced by secondary muscovite. Oscillatory zoning and twinning are visible in few crystals. Quartz (c. 30 %) forms anhedral crystals, which are commonly recrystallised to mosaics of smaller crystals. K-feldspar (c. 25 %) crystals commonly show microcline twinning or perthitic exsolution. Generally fresh, strongly pleochroic (beige to dark brown or green) biotite (5 %) occurs as lath-shaped phenocrysts, in interstices, and in the matrix. Muscovite is predominantly present as primary lath-shaped crystals that are up to 2.5 mm long and in interstices; secondary muscovite can be found replacing plagioclase (total muscovite c. 5 %).

#### *2.2.2. The Cove Granite*

The Cove Granite crops out over an area of 2 km along the coastal cliffs south of Cove. The contact with the surrounding migmatised country rocks is mostly gradational, but at its southern margin it intruded the country rocks in sheet-like apophyses (Munro, 1986). Biotite clusters and schlieren, which may represent restitic material, as well as pegmatites and quartz veins, are common features.

The unfoliated Cove Granite is dark-grey in colour, fine- to medium-grained (< 1-3.5 mm) and shows an equigranular to weakly inequigranular texture. Plagioclase (c. 30 %), which forms up to 2.5 mm long crystals is typically strongly altered to sericite and replaced by secondary muscovite. Quartz (c. 30 %) predominantly occurs as crystals that are approximately 2.5 mm long, but also in interstices; it is typically strained and shows development of subgrains. K-feldspar (c. 25 %), which forms the largest crystals (up to 3.5 mm) always displays microcline twinning. Pleochroic (beige to dark brown or dark green) biotite (c. 15 %, up to 2 mm) is mostly evenly distributed in thin section, but has also been observed in small possibly restitic biotite

clusters in hand specimen. Muscovite makes up only c. 5 % of the mineral assemblage and is always fine-grained (c. 1 mm). Some may be primary, but most is secondary and replaces plagioclase.

### *2.2.3. The Nigg Bay Granite*

The Nigg Bay Granite is by far the smallest of the three S-type granites, but as it grades into the surrounding strongly migmatized country rocks and contains a high proportion of country rock xenoliths, a reliable estimate of its size cannot be given. Large biotite clots (several cm) and biotite schlieren are common, and in places the original metamorphic fabric is still visible. In addition, a weak magmatic foliation (defined by biotite) may be observed.

The Nigg Bay Granite is dark-grey in colour and has an inequigranular (predominantly < 0.5-4 mm) to porphyritic texture in which plagioclase, K-feldspar and quartz phenocrysts may be up to 1 cm in size. Plagioclase (c. 30 %) is commonly altered, but not as extensively as in the Kemnay and Cove granites, and some crystals show oscillatory zoning. Quartz (c. 30 %) is always strained and K-feldspar (c. 20 %) displays microcline twinning. In contrast to the Kemnay and Cove granites, biotite in the Nigg Bay Granite (15 %) displays red-brown to dark-brown pleochroism. It mostly occurs in clusters with muscovite and has a maximum size of 2 mm. Muscovite (5 %) is predominantly secondary, occurs in clusters with biotite and most often in plagioclase.



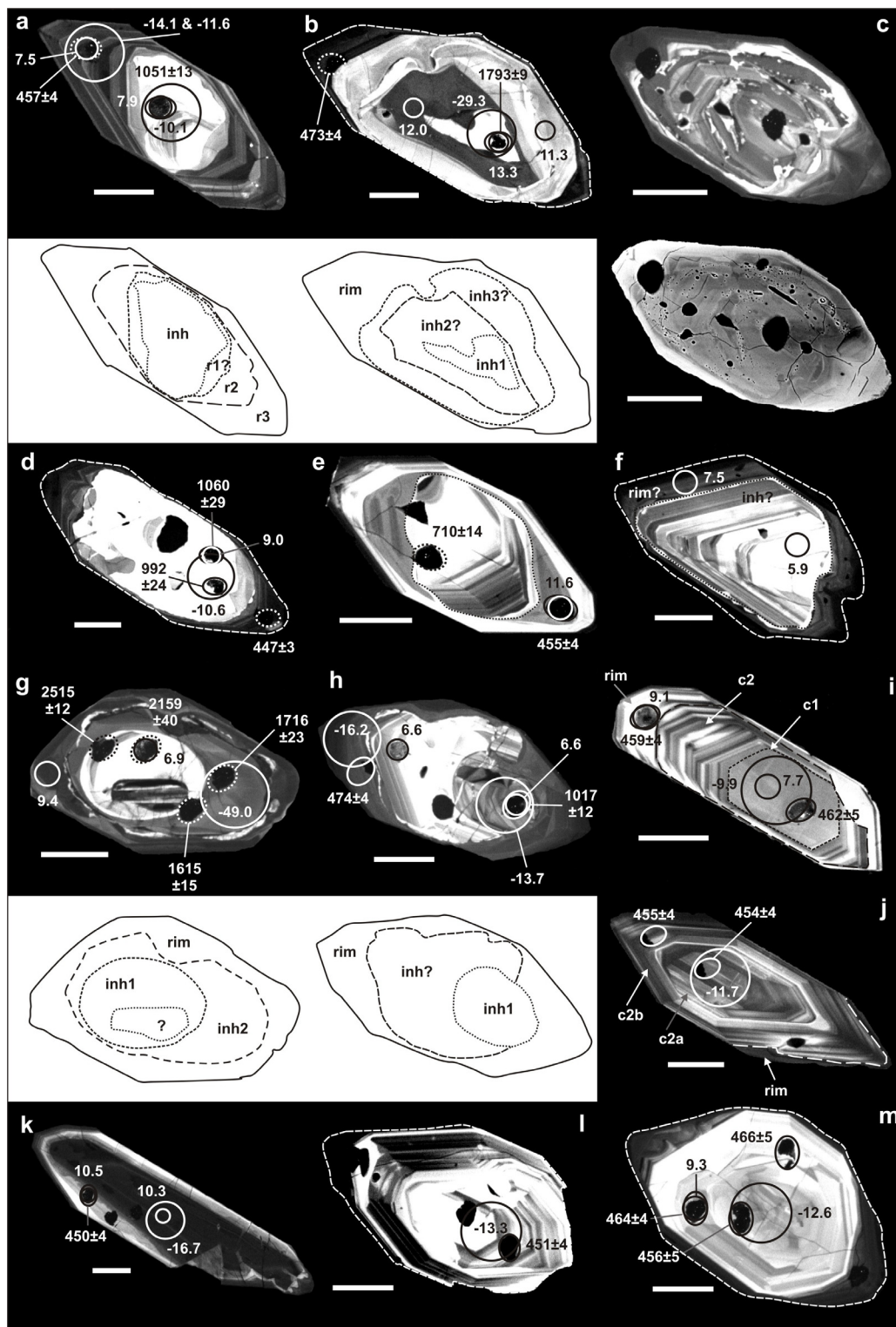


Fig. 2: SEM images of representative inherited and magmatic zircons from the Kemnay, Cove and Nigg Bay granites

- a) Zircon comprising strongly luminescent oscillatory zoned inherited core and oscillatory zoned rims (Kemnay, grain 23).
  - b) Zircon with an inherited core showing an oxygen isotope composition of  $13.3 \pm 0.6$  ‰ in the inner part,  $12.0 \pm 0.6$  ‰ in the outer part of the core and  $11.3 \pm 0.6$  ‰ in the rim (Kemnay, grain 35).
  - c) CL and BSE images of zircon crystal with large inherited core showing porous, mottled texture (Cove, grain 16).
  - d) Zircon with unzoned, strongly luminescent inherited core and oscillatory zoned weakly luminescent rim (Cove, grain 9).
  - e) Zircon with oscillatory zoned and strongly to moderately luminescent inherited core and multiple rims (Cove, grain 12).
  - f) Zircon crystal comprising an inherited core and magmatic rim representative of the Nigg Bay Granite. Note the variation in  $\delta^{18}\text{O}$  between the inherited core ( $5.9 \pm 0.6$  ‰) and the magmatic rim ( $7.5 \pm 0.6$  ‰) (Nigg Bay, grain 19).
  - g) Zircon comprising an inherited inner resorbed, unzoned, strongly luminescent core, an inherited outer resorbed, unzoned, moderately luminescent zone and a convoluted weakly luminescent magmatic rim (Cove, grain 20). Note the large variation in  $\delta^{18}\text{O}$  between the inherited component ( $6.9 \pm 0.6$  ‰) and the magmatic rim ( $9.4 \pm 0.6$  ‰).
  - h) Zircon crystal comprising an inherited core and magmatic rim representative of the Nigg Bay Granite (grain 31).
  - i) Magmatic zircon with a moderately luminescent unzoned inner core domain, an outer oscillatory zoned domain and, separated by a resorption surface, a thin outer weakly luminescent rim (Kemnay, grain 9). Note the large difference in  $\delta^{18}\text{O}$  between the inner core ( $7.7 \pm 0.6$  ‰ ( $2\sigma$ )) and rim ( $9.1 \pm 0.6$  ‰).
  - j) Magmatic zircon crystal with zoned core and oscillatory narrowly zoned rim (separated by strongly luminescent resorption surface) (Kemnay, grain 40).
  - k) Magmatic zircon with large weakly luminescent unzoned core and oscillatory zoned rim (Cove, grain 7).
  - l) Magmatic zircon comprising a strongly luminescent unzoned inner core domain, zoned outer core domain and multiple oscillatory zoned rims (Cove, grain 14).
  - m) Magmatic zircon with strongly luminescent oscillatory zoned core and weakly luminescent rim (Cove, grain 5).
- (scale bar = 50  $\mu\text{m}$ ; small circles indicate ion probe pit of oxygen isotope analysis, ellipse of U-Pb analysis and large circle of laser Hf isotope analysis; precision of  $\delta^{18}\text{O}$  = 0.6 ‰ ( $2\sigma$ ), of  $\epsilon\text{Hf}$  = on average 1.1 units).

### 3. Samples

As this study has to be considered a pilot study only one sample of the Kemnay, Cove and Nigg Bay granites was chosen for analysis. Zircon crystals in the Kemnay, Cove and Nigg Bay granites are 100-400  $\mu\text{m}$  long and typically stubby; only a few are markedly elongate. In the Kemnay and Cove granites approximately 60 % of crystals, and c. 90-95 % of crystals in the Nigg Bay Granite, comprise a large older inherited core and a narrow weakly or moderately luminescent oscillatory-zoned magmatic rim interpreted to have grown from the granite magma. Zircon crystals commonly contain numerous cracks, and sometimes have a porous, mottled texture, hence poor grain quality.

In the Kemnay Granite inherited cores are commonly more strongly luminescent (Fig. 2a), and in some cases oscillatory zoning is visible. Crystals without an older inherited component are broadly of two types: some comprise a moderately luminescent unzoned inner core domain, an outer oscillatory zoned domain with narrow zones of varying CL intensities and, separated by an obvious resorption surface, a thin outer weakly luminescent rim (Fig. 2i); others consist of an oscillatory-zoned core, a first narrowly zoned rim of similar CL intensity to the core, and a second weakly luminescent rim (Fig. 2j).

In the Cove and Nigg Bay granites crystals with inherited cores display a range of textures and CL intensities. Zoning patterns are commonly complex (Fig. 2b-h), and in at least one crystal multiple inherited components of differing age were found (Fig. 2g). Similarly, magmatic crystals are texturally more variable and do not show any systematic patterns (Fig. 2k-m).

#### **4. Methodology**

Major and trace elements were determined at the University of Edinburgh using a PW2404 wavelength-dispersive sequential X-ray spectrometer. Rare earth elements (REEs) and some trace elements (Y, Hf, Th, U) were analysed at the British Geological Survey (BGS) in Nottingham. Zircon separation followed conventional methods and was carried out in the University of St. Andrews Mineral Separation Facility.

Zircon oxygen isotope data were obtained using a Cameca ims-1270 at the Edinburgh Ion Microprobe Facility (EIMF). The method closely followed that of Cavosie et al. (2005), Kemp et al. (2006). Subsequent to oxygen isotope analyses, U-Th-Pb analyses were carried out also using the Cameca ims-1270 at the EIMF. Analytical procedures are similar to those described by Schuhmacher et al. (1994) and Whitehouse et al. (1997), and are described in detail in Kelly et al. (accepted).

Hafnium isotope analysis was carried out at the NERC Isotope Geosciences Laboratory (NIGL) in Nottingham, using a Nu Instruments Nu-Plasma HR multi-collector ICP-MS coupled to a New Wave Research UP193SS 193nm solid state

laser ablation system (a summary data table can be found in Table 1; detailed analytical protocols and full data sets are in Appendices 4a-4f).

## 5. Results

### 5.1. Zircon U-Pb data

#### 5.1.1. The Kemnay Granite

Twenty-four zircon crystals from the Kemnay Granite were dated by U-Pb analysis; of these thirteen crystals contain an older inherited core. Magmatic grains and magmatic rims yield a weighted average  $^{206}\text{Pb}/^{238}\text{U}$  age of  $457 \pm 3$  Ma (n=10) (Fig. 3a). Ten concordant inherited zircons give  $^{207}\text{Pb}/^{206}\text{Pb}$  ages of  $1047 \pm 19$  Ma (weighted average age, n=3),  $1442 \pm 13$  (weighted average age, n=3),  $1473 \pm 16$  Ma (n=1),  $1525 \pm 11$  Ma (n=1),  $1740 \pm 9$  Ma (n=1) and  $1793 \pm 9$  Ma (n=1). Discordant inherited zircons yield minimum  $^{207}\text{Pb}/^{206}\text{Pb}$  ages of  $794 \pm 22$  Ma,  $899 \pm 23$  Ma,  $997 \pm 19$  Ma,  $1352 \pm 11$  Ma,  $1417 \pm 9$  Ma and  $2556 \pm 24$  Ma (all n=1) (Fig. 3b).

#### 5.1.2. The Cove Granite

Magmatic cores and rims have a weighted average  $^{206}\text{Pb}/^{238}\text{U}$  age of  $458 \pm 5$  Ma (n=10) (Fig. 3c). Ten out of eighteen analysed crystals have an inherited core. However, only four analyses of these yield concordant  $^{207}\text{Pb}/^{206}\text{Pb}$  ages, of  $992 \pm 24$  Ma,  $1060 \pm 29$  Ma,  $1158 \pm 32$  Ma and  $1472 \pm 7$  Ma (Fig. 3d). Three discordant analyses yield minimum  $^{207}\text{Pb}/^{206}\text{Pb}$  ages of  $702 \pm 79$  Ma,  $1716 \pm 23$  Ma,  $2159 \pm 40$  Ma,  $2515 \pm 12$  Ma and  $2685 \pm 6$  Ma.

#### 5.1.3. Nigg Bay Granite

Seven analyses of magmatic rims give a weighted average  $^{206}\text{Pb}/^{238}\text{U}$  age of  $465 \pm 5$  Ma (n=7) (Fig. 3e). Inherited components were identified in thirteen out of fifteen analysed grains, which have concordant  $^{207}\text{Pb}/^{206}\text{Pb}$  ages of  $919 \pm 10$  Ma (n=1),  $997 \pm 22$  Ma (weighted average age, n=4),  $1136 \pm 31$  Ma (weighted average age, n=2) and  $1600 \pm 6$  Ma (n=1) (Fig. 3f).

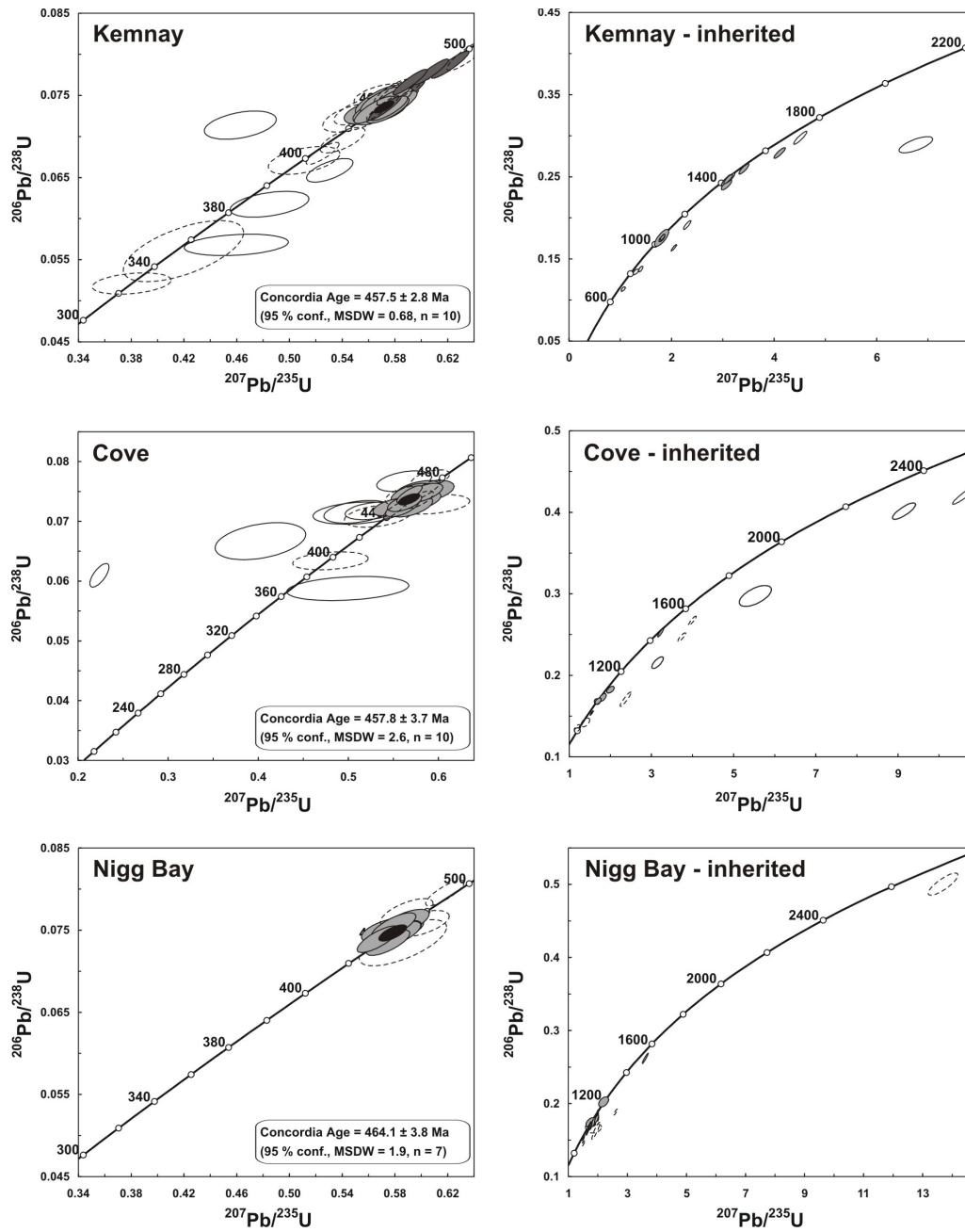


Fig. 3: Concordia diagrams of magmatic zircons and pre-magmatic inherited cores. Grey ellipses represent concordant, white ellipses discordant, white dashed ellipses rejected data points. Data point error ellipses are  $2\sigma$ .

low- $\delta^{18}\text{O}$  component, possibly hydrothermally altered, supracrustal rocks or a mafic infracrustal source. Thus, this pilot study of S-type granites shows that, while field and whole-rock geochemical data have been interpreted to suggest simple melting of supracrustal sources, S-type granites, like I-type granites, may have complex petrogenetic histories and may comprise a mixture of supracrustal  $\pm$  infracrustal sources.

**Table 1**  
**Summary of zircon U-Pb, O and Hf isotope data**

sample	U-Pb age [Ma]	2 $\sigma$	n	$\delta^{18}\text{O}$ [‰]	2 $\sigma$	n	$\epsilon_{\text{Hf}}$	95% conf.	TDM <sub>c</sub> [Ma]	95% conf.	n
<u>Kemnay</u>											
magmatic	457	3	10	9.2	(7.0-12.0)	0.6	19	-13.1 (-9.9 to -17.3)	2066-2531	1.1	67
inherited (concordant)	1047-1793	30	10	10.5	(6.7-13.3)	0.6	8	-19.7 (-9.0 to -29.3)	1647-2456	0.9	64
inherited (discordant)	794-2556	36	6								
<u>Cove</u>											
magmatic	458	5	10	10.0	(8.8-11.6)	0.6	6	-15.4 (-12.6 to -20.3)	2234-2718	0.9	54
inherited (concordant)	992-1472	46	3	7.6	(6.9-9.0)	0.6	3	-30.5 (-10.6 to -49.0)	1796-3737	0.8	59
inherited (discordant)	702-2685	55	3								
<u>Nigg Bay</u>											
magmatic	465	5	7	7.3	(6.1-8.4)	0.6	7	-15.6 (-12.2 to -18.5)	2217-2609	0.9	52
inherited (concordant)	919-1600	40	8	6.0	(4.1-9.7)	0.6	16	-11.3 (-9.5 to -13.7)	1662-2310	1.0	74

## 5.2. Zircon oxygen isotope data

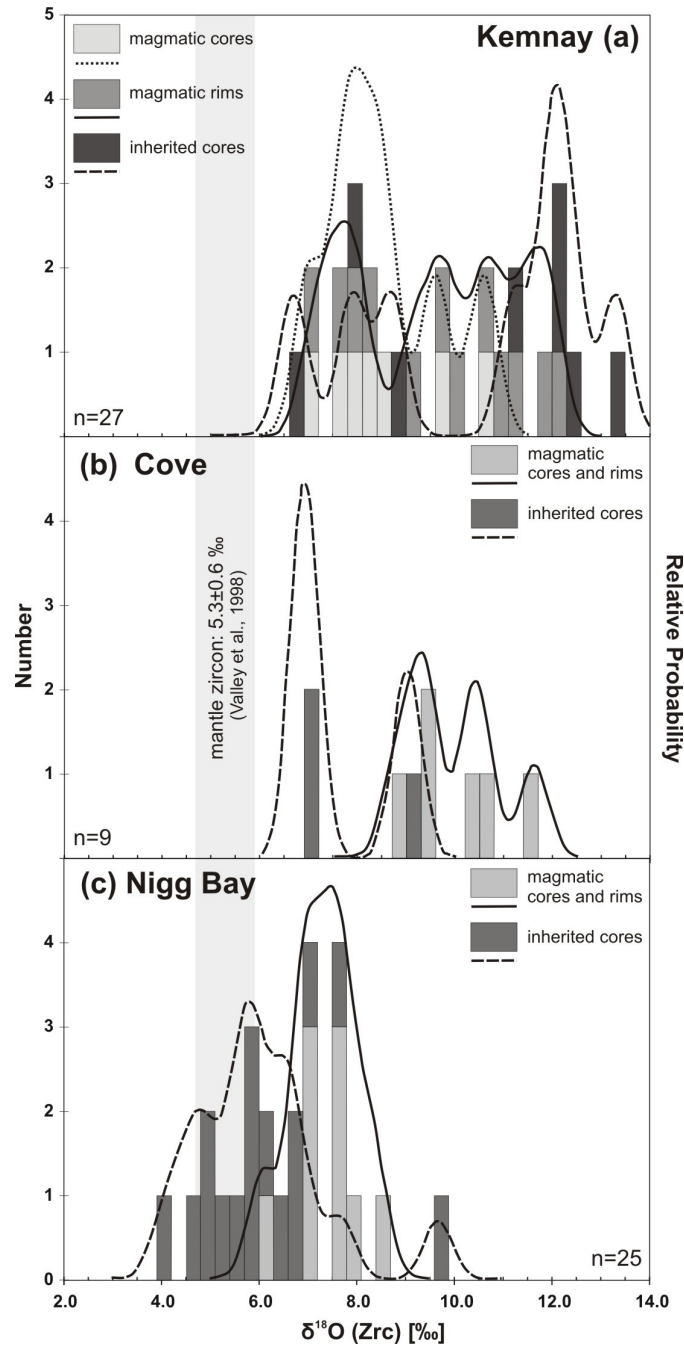


Fig. 4: Cumulative probability plots of zircon oxygen isotope data (probability curves and histograms were calculated at  $1\sigma$ ).



### 5.2.1. The Kemnay Granite

Magmatic zircons of the Kemnay Granite have a mean oxygen isotope composition of  $9.2 \pm 3.2$  ‰ (2SD; n=19; 7 magmatic cores and 12 rims) and range from 7.0 ‰ to 12 ‰. For comparison, zircon standard 91500 analysed in the same analytical session shows a 2SD uncertainty of  $\pm 0.6$  ‰, which approximates the external analytical precision. Some systematic differences exist between magmatic cores and rims (Fig. 4a). Magmatic cores display predominantly low  $\delta^{18}\text{O}$  values with a mean of  $8.6 \pm 2.4$  ‰, whereas rims cover the entire range and therefore have a mean  $\delta^{18}\text{O}$  value close to the overall sample mean ( $9.6 \pm 3.4$  ‰). Inherited zircons display the highest mean ( $10.5 \pm 4.8$  ‰; n=8) and show the largest spread between 6.7 ‰ and 13.3 ‰.

Multiple analyses were made on four magmatic zircon crystals and five crystals comprising an older inherited core. Of these only one magmatic grain (Fig. 2i) and one inherited grain (Fig. 2b) show resolvable intra-grain variations. The magmatic crystal has a core of 7.7 ‰ and a rim of 9.1 ‰; the crystal comprising an inherited core shows a  $\delta^{18}\text{O}$  value of 13.3 ‰ in the inner part of the core, 12.0 ‰ in the outer part and 11.3 ‰ in the rim.

### 5.2.2. The Cove Granite

Magmatic zircon cores and rims have a mean  $\delta^{18}\text{O}$  value of  $10.0 \pm 2.0$  ‰ (2SD, n=6 = 2 cores and 4 rims) (analytical precision = 0.6 ‰ (2 $\sigma$ )). Cores and rims have, within error, the same oxygen isotope composition (cores:  $9.8 \pm 1.4$  ‰; rims:  $10.1 \pm 2.5$  ‰) (Fig. 4b) assuming that this small number of analyses is representative. However, inherited cores are generally less enriched in  $^{18}\text{O}$  with a mean  $\delta^{18}\text{O}$  value of  $7.6 \pm 2.4$  ‰ (n=3). Poor zircon grain quality (cracks, high common Pb, discordance etc.) resulted in many data being rejected, and reliable values for core-rim pairs were obtained from only two crystals. One of these, a wholly magmatic crystal displays no  $\delta^{18}\text{O}$  variation between core and rim (Fig. 2k), whereas the other displays a large difference (inherited core of 6.9 ‰; magmatic rim of 9.4 ‰) (Fig. 2g; grain 20).

### 5.2.3. The Nigg Bay Granite

Magmatic zircon rims of the Nigg Bay Granite form a unimodally distributed, relatively tight data cluster (Fig. 4c) with a mean oxygen isotope composition of  $7.3 \pm 1.4$  (2SD, n=9) (analytical precision  $\pm 0.6$  ‰ (2 $\sigma$ )). Inherited cores show  $\delta^{18}\text{O}$  values between 4.1 ‰ and 7.7 ‰ (one outlier at 9.7 ‰) and a mean of  $5.8 \pm 2.0$  (n=15). Resolvable variation between inherited cores and magmatic rims was discovered in one (Fig. 2f) out of four grains where core-rim analyses were carried out. In this crystal (grain 19) the inherited core has a lower  $\delta^{18}\text{O}$  value (5.9 ‰) than the rim (7.5 ‰).

## 5.3. Zircon Hf isotope data

### 5.3.1. The Kemnay Granite

Initial  $\epsilon\text{Hf}$  values for magmatic zircons lie between  $-9.9 \pm 1.6$  and  $-17.3 \pm 1.9$  (quoted errors = 95 % confidence level) (Fig. 5a), with a mean of  $-13.1 \pm 4.4$  (2SD, n=11) and a range of 7.4  $\epsilon\text{Hf}$  units. Equivalent two-stage Hf model ages, calculated based on the  $^{176}\text{Lu}/^{177}\text{Hf}$  ratio of the average crust ( $^{176}\text{Lu}/^{177}\text{Hf} = 0.015$ , Griffin et al., 2002), range from  $2066 \pm 95$  to  $2531 \pm 116$  Ma (Fig. 5b). Due to a laser spot size of 50  $\mu\text{m}$  and poor zircon grain quality, it was not possible to carry out multiple analyses on magmatic rims or on magmatic crystals. However, the time-resolved signal revealed a decrease in  $\epsilon\text{Hf}$  value from  $-14.1 \pm 0.9$  to  $-11.6 \pm 1.8$  in one crystal (grain 23, Fig. 2a), which suggests that some intra-grain variation does exist.

Initial  $\epsilon\text{Hf}$  values of inherited zircons range from  $+5.2 \pm 1.1$  (grain 31, U-Pb age =  $1525 \pm 11$  Ma) to  $-2.5 \pm 1.3$  (grain 33, U-Pb age =  $1473 \pm 16$  Ma) (Fig. 5a); Hf model ages vary between  $1647 \pm 61$  Ma (grain 26, U-Pb age =  $1047 \pm 19$  Ma) and  $2456 \pm 59$  Ma (grain 35, U-Pb age =  $1793 \pm 9$  Ma) (Fig. 5c). Re-calculated to 457 Ma,  $\epsilon\text{Hf}$  values lie between  $-9.0 \pm 0.8$  (grain 26, U-Pb age =  $1047 \pm 19$  Ma) and  $-29.3 \pm 0.8$  (grain 35, U-Pb age =  $1793 \pm 9$  Ma).

### 5.3.2. The Cove Granite

Initial  $\epsilon\text{Hf}$  values for magmatic zircon lie between  $-12.6 \pm 0.9$  to  $-20.3 \pm 1.1$  (Fig. 5a), with a mean of  $-15.4 \pm 5.1$  (2SD, n=7) and a range of 7.7  $\epsilon\text{Hf}$  units. Hf model

ages range from  $2234 \pm 52$  Ma to  $2718 \pm 62$  Ma (Fig. 5b). Inherited zircons display initial  $\epsilon\text{Hf}$  values of  $+2.5 \pm 1.3$  (grain 17, U-Pb age =  $1158 \pm 32$  Ma),  $+0.7 \pm 1.0$  (grain 9, U-Pb age:  $972 \pm 11$  Ma) and  $-21.0 \pm 1.2$  (grain 20, U-Pb age:  $1716 \pm 23$  Ma) (Fig. 5a). At 458 Ma  $\epsilon\text{Hf}$  values are  $-10.6 \pm 0.9$ ,  $-12.9 \pm 0.8$  and  $-49.0 \pm 0.8$ , respectively, and equivalent Hf model ages are  $1796 \pm 55$  Ma,  $1825 \pm 62$  Ma and  $3737 \pm 59$  Ma (Fig. 5c).

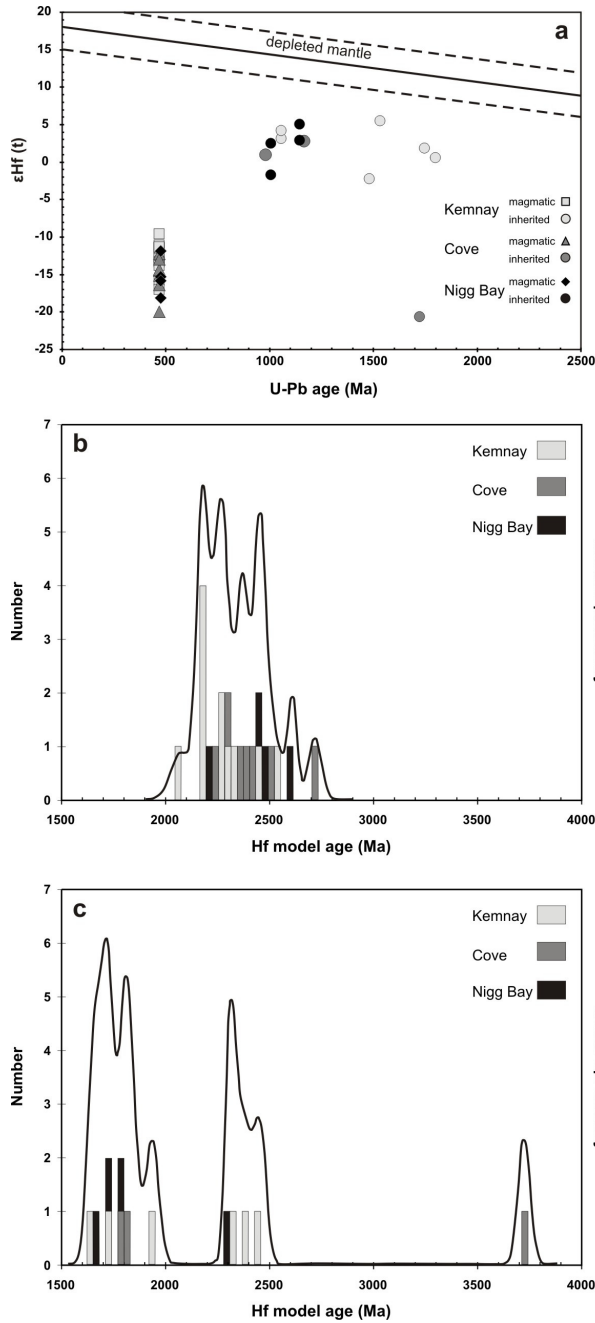


Fig. 5a) U-Pb ages vs. initial  $\epsilon\text{Hf}$  values of magmatic and inherited zircons of the Kemnay, Cove and Nigg Bay granites; b) Hf model ages (calculated using average continental crust  $^{176}\text{Lu}/^{177}\text{Hf} = 0.015$ ) of magmatic zircons of the Kemnay, Cove and Nigg Bay granites; c) Hf model ages (calculated using average continental crust  $^{176}\text{Lu}/^{177}\text{Hf} = 0.015$ ) of inherited zircons of the Kemnay, Cove and Nigg Bay granites.

### 5.3.3. The Nigg Bay Granite

Magmatic zircons of the Nigg Bay Granite show a spread of 6.3 initial  $\epsilon\text{Hf}$  units between  $-12.2 \pm 1.0$  and  $-18.5 \pm 0.7$  (Fig. 5a), a mean value of  $-15.6 \pm 5.2$  (2SD,  $n=4$ ) and Hf model ages between  $2217 \pm 58$  Ma and  $2609 \pm 43$  Ma (Fig. 5b).

Four inherited cores with U-Pb ages of  $997 \pm 22$  Ma ( $n=2$ ) and  $1136 \pm 31$  Ma ( $n=2$ ) show initial  $\epsilon\text{Hf}$  values between  $+4.8 \pm 1.4$  and  $-2.0 \pm 1.1$  (Fig. 5a). At 465 Ma  $\epsilon\text{Hf}$  values vary between  $-9.5 \pm 0.8$  (grain 25, U-Pb age =  $1136 \pm 31$  Ma) and  $-13.7 \pm 0.8$  (grain 31, U-Pb age =  $997 \pm 22$  Ma). Hf model ages range from  $1662 \pm 67$  Ma (grain 25) to  $2310 \pm 44$  Ma (grain 31) (Fig. 5c).

## 6. Discussion

### 6.1. Origin and evolution of the Kemnay, Cove and Nigg Bay granites

Zircon crystals in all three granites display a similar range of highly evolved  $\epsilon\text{Hf}$  values, typical of ancient continental crust (full range  $-9.9$  to  $-20.3$ ; Fig. 5a). For comparison, contemporary depleted mantle has an  $\epsilon\text{Hf}$  value of approximately  $+16 \pm 3$  (Vervoort and Blichert-Toft, 1999). Hf model ages calculated for magmatic and inherited zircon in all three granites are much older than equivalent U-Pb ages, and range from 2.7 to 2.05 Ga in magmatic zircon (Fig. 5b), and from 2.5 Ga and 1.65 Ga (one outlier of 3.75 Ga in the Cove Granite) in inherited zircon (Fig. 5c). Hf model ages are strongly dependent on the  $^{176}\text{Lu}/^{177}\text{Hf}$  ratio used in the calculation, and hence should be considered very rough estimates of the time of separation from the mantle. For example, using the  $^{176}\text{Lu}/^{177}\text{Hf}$  ratio of the granite host ( $^{176}\text{Lu}/^{177}\text{Hf} = 0.003\text{--}0.004$ ) instead of the average crust ( $^{176}\text{Lu}/^{177}\text{Hf} = 0.015$ ; Griffin et al., 2002) results in Hf model ages that are approximately 500 million years younger than those above. The fact that inherited cores have younger model ages than their magmatic rims (with the exception of one inherited core in the Cove Granite, which gave an unrealistic model age of 3.75 Ga) suggests that the  $^{176}\text{Lu}/^{177}\text{Hf}$  ratio of the average crust is not representative here. The actual  $^{176}\text{Lu}/^{177}\text{Hf}$  value(s) of the granite protolith(s) probably lies somewhere between that of the average crust and the host

rock, and may have changed with time as Lu and Hf fractionate during magmatic processes (Nebel et al., 2007). Though the above Hf model ages may not reflect the exact crustal residence ages of protoliths, the data demonstrate that the granite magmas recycled old crust and contain no evidence of a contemporary depleted mantle component.

The absence of published Hf isotope data for Dalradian strata precludes a direct comparison with the granite zircon Hf isotope data. However, several  $\epsilon\text{Nd}$  values for the Dalradian have been published from which equivalent  $\epsilon\text{Hf}$  values can be calculated using the terrestrial array Hf-Nd correlation ( $\epsilon\text{Hf} = \epsilon\text{Nd} * 1.36 + 3$ ) of Vervoort et al. (1999). Using the  $\epsilon\text{Nd}$  values of Frost et al. (1983) and Frost and O’Nions (1985), calculated at 460 Ma, equivalent  $\epsilon\text{Hf}$  values range from -6.1 to -14.0 for the Appin Group (outlier at -27.9;  $\epsilon\text{Nd} = -6.7$  to -12.5), -16.9 to -27.7 for the Argyll Group ( $\epsilon\text{Nd} = -14.6$  to -22.6), and -20.1 to -23.7 for the Southern Highland Group ( $\epsilon\text{Nd} = -17.0$  to -19.6). Thus, magmatic zircons from the Kemnay, Cove and Nigg Bay granites have similar Hf isotope compositions to rocks from the Appin and Argyll groups. In addition, U-Pb age data of inherited zircons found in the granites, which range from c. 1.8 Ga to 1.05 Ga in Kemnay, c. 1.5 Ga to 1.0 in Cove, and 1.6 Ga to c. 0.9 Ga in Nigg Bay, and define dominant peaks at c. 1.05-1.0 Ga and c. 1.45 Ga (discordant age data define an additional small peak at c. 2.7-2.5 Ga) (Fig. 6), are in good agreement with SHRIMP data of detrital zircon from the Grampian, Appin, Argyll and Southern Highland groups of the Dalradian Supergroup (Cawood et al., 2003). The similar Hf isotope compositions between rocks of the Dalradian Supergroup and the granites’ magmatic zircons, together with the similar age spectra yielded by inherited and detrital zircon, strongly suggest a Dalradian source and most likely exactly the same source for the magmas, which is consistent with field evidence.

In contrast, large differences exist between the Kemnay, Cove and Nigg Bay granites regarding the oxygen isotope compositions of their magmatic and inherited zircons (Fig. 4). Currently, there are no zircon oxygen isotope data for other Scottish S-type granites, but published whole-rock values (Aberchirder, Aberdeen, Auchedly, Glencroft, Kemnay, Kilmelford, Loch Laggan, Strathspey, Strichen) lie between 9.2 ‰ and 12.1 ‰, with the majority lying above 10 ‰ (Halliday, 1984; Hamilton et al.,

1980; Harmon, 1983; Kay, 1980). Assuming equilibrium between zircons and their host rocks and an oxygen isotope fractionation factor ( $\Delta(\text{WR-Zrc})$ ) of approximately 1.8 at c. 70 wt%  $\text{SiO}_2$  (Valley et al., 2005), zircon  $\delta^{18}\text{O}$  values should range from 7.4–10.3 ‰. Magmatic zircons of the Kemnay and Cove granites show mean values of 9.2 ‰ and 10.0 ‰, typical of S-type granites. However, magmatic zircons of the Nigg Bay Granite have a lower mean  $\delta^{18}\text{O}$  value (7.3 ‰), similar to those found in I-type granites (e.g. Paper 2). Inherited zircons from the Nigg Bay Granite display even lower  $\delta^{18}\text{O}$  values (4.1–7.7 ‰, mean = 5.8 ‰) with the majority lying within and even below the field of values for mantle-like zircon ( $5.3 \pm 0.6$  ‰, Valley et al., 1998) (Fig. 4c). Thus, even though field, whole-rock geochemical and Hf isotope data for magmatic zircon, and U-Pb isotope data for inherited zircon all provide strong evidence for involvement of a only supracrustal sources in the Kemnay, Cove and Nigg Bay granites, zircon oxygen isotope data show that at least the Nigg Bay Granite contains either additional or entirely different source material.

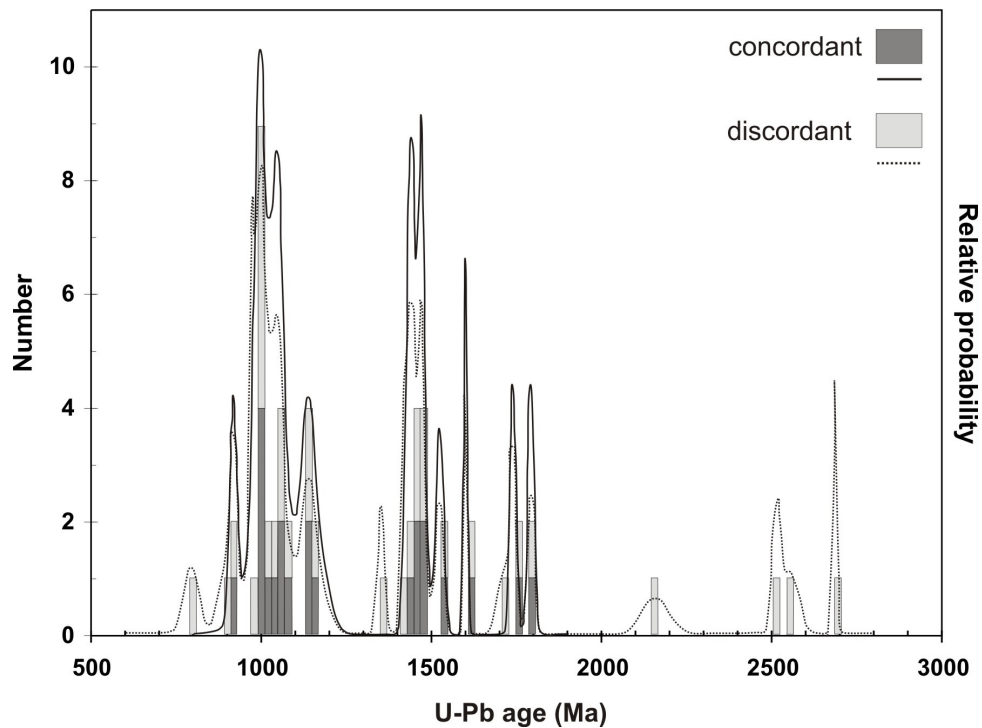


Fig. 6: U-Pb ages of concordant and discordant inherited zircons found in the Kemnay, Cove and Nigg Bay granites.

Combined  $\delta^{18}\text{O}$  and  $\epsilon\text{Hf}$  data for magmatic and inherited zircon in the Kemnay, Cove and Nigg Bay granites define two near-parallel trends; one trend is defined by zircons from the Cove and Kemnay granites, and at lower  $\delta^{18}\text{O}$  values a second trend is defined by zircons from the Nigg Bay Granite. These trends indicate mixing between at least two components in the granites (Fig. 7). Comparison with published whole-rock oxygen and calculated Hf isotope data for rocks of the Appin, Argyll and Southern Highland groups (Anderson et al., 2004; Frost and O’Nions, 1985; O’Nions et al., 1983) shows good agreement for the Kemnay and Cove granites with those of the Appin Group and to a lesser extent with those of the Argyll Group. Zircons from the Nigg Bay Granite furthermore overlap the field defined by mantle-like zircons.

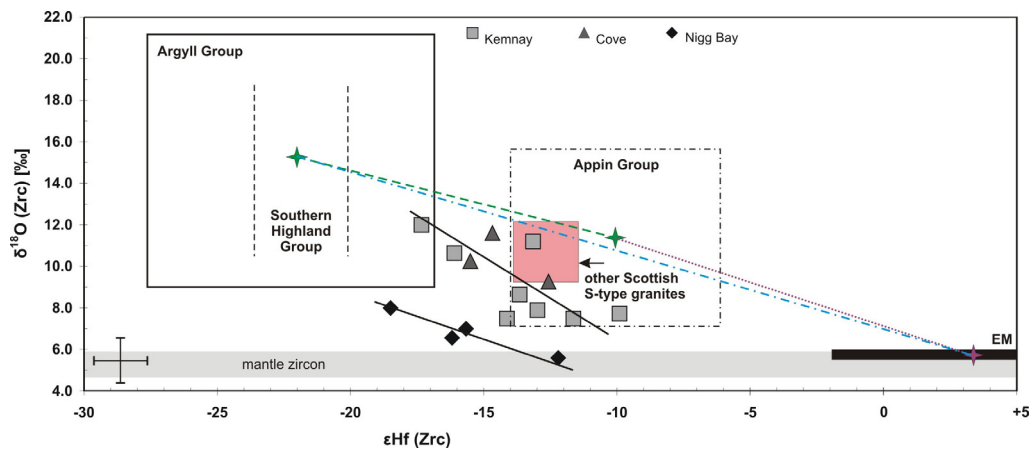


Fig. 7:  $\epsilon\text{Hf}$  values (at emplacement age) vs.  $\delta^{18}\text{O}$  of magmatic zircons of the Kemnay, Cove and Nigg Bay granites (precision on zircon  $\delta^{18}\text{O}$  and  $\epsilon\text{Hf}$  = 0.6 ‰ and 1.0 units ( $2\sigma$ ), respectively). Also shown are fields for whole-rock  $\delta^{18}\text{O}$  and estimated  $\epsilon\text{Hf}$  data of the Appin, Argyll and Southern Highland groups, and other Scottish S-type granites (data from Anderson et al., 2004; Frost and O’Nions, 1985; Halliday, 1984; Hamilton et al., 1980; Harmon, 1983; Kay, 1980; O’Nions et al., 1983) and mixing lines (green, purple and blue) between the potential end-members.

Based on these trends three possible petrogenetic models may be proposed for the Kemnay, Cove and Nigg Bay granites: (1) The granites formed by melting of a large proportion of Appin Group and a smaller proportion of Argyll ± Southern Highland Group rocks. Simple two-component magma mixing modelling indicates that zircon  $\delta^{18}\text{O}$  values of the Kemnay Granite may represent mixing between 35-100 % Appin and 65-0 % Argyll rocks; this ratio changes to 45-100 % Appin and 0-55 % Argyll rocks in the Cove Granite. If field evidence suggesting that the granites were

generated more or less in situ is valid, the low- $\delta^{18}\text{O}$  values in magmatic and inherited zircon in the Nigg Bay Granite represent a local low- $\delta^{18}\text{O}$ , possibly hydrothermally altered, component within the Appin or Argyll groups. (2) Only the Kemnay and Cove granites were generated by melting of Appin Group and Argyll  $\pm$  Southern Highland Group rocks. The Nigg Bay Granite formed by mixing between Argyll  $\pm$  Southern Highland Group rocks and an unknown infracrustal source with mantle-like oxygen and crustal Hf isotope characteristics or by mixing with enriched mantle. Based on magma mixing modelling 20-50 % of a mantle-like component may be present in the Nigg Bay Granite. (3) Neither granite involved melting of Appin Group rocks, and all formed by different degrees of mixing between Argyll  $\pm$  Southern Highland Group rocks and an infracrustal source. In order to produce the observed zircon  $\delta^{18}\text{O}$  values of the Kemnay and Cove granites 15-65 % of a mantle-like component has to have been incorporated into the supracrustal source rocks.

Several models have been proposed for the nature, age and affinity of the lower crust below the Grampian Highlands, but since appropriate rocks are not exposed in this part of Scotland, these are based on geophysical constraints, geochemical and isotopic data for the late Caledonian granites, U-Pb ages of inherited zircons from the late Caledonian I-type granites and wider geological arguments. Recently, an integrated oxygen, U-Pb and Hf isotope study of zircon in Scottish late Caledonian I-type granites provided evidence that the basement beneath the Grampian Highlands represents a complicated mixture of Archaean- to Neoproterozoic-age material (Paper 3). It may therefore be that the Nigg Bay Granite, and to a lesser extent the Kemnay and Cove granites, comprise mixtures of infracrustal sources rather than one single source.

In addition to varying  $\delta^{18}\text{O}$  values for magmatic and inherited zircon in the Kemnay, Cove and Nigg Bay granites, the data also differ in the degree of oxygen isotope heterogeneity. An explanation for this may be found in the different body sizes and in the degree of mixing. The Kemnay Granite, by far the largest of the three, shows a 5 ‰ variation in magmatic zircon  $\delta^{18}\text{O}$  and an even larger spread amongst inherited zircons, whereas the much smaller Cove and Nigg Bay granites display considerably smaller variation (c. 2.5 ‰). The large heterogeneity observed in the Kemnay Granite may result from melting a much larger, and therefore



potentially isotopically more variable, volume of material. Furthermore, inefficient mixing in the Kemnay Granite in contrast to thorough mixing in the isotopically more homogenous Cove and Nigg Bay granites may have also played a role.

### *6.2. Emplacement of the Kemnay, Cove and Nigg Bay granites*

Few reliable ages constrain crystallisation of the Caledonian S-type granites, but published data suggest that those of the northeastern Grampian Highlands crystallised between c. 470 Ma and 465 Ma (Strichen  $467 \pm 6$  Ma (zircon, Oliver, 2001); Aberdeen  $470 \pm 1$  Ma (monazite, Kneller and Aftalion, 1987)). A Rb/Sr mineral age (no isochron) of  $411 \pm 7$  Ma published for the Kemnay Granite (Bell, 1968) is unlikely to be reliable. The new SIMS U-Pb zircon ages for the Kemnay, Cove and Nigg Bay granites ( $457 \pm 3$  Ma,  $458 \pm 5$  Ma and  $465 \pm 5$  Ma, respectively) show them to be essentially post-tectonic with respect to the peak Grampian Event deformation (D2) and metamorphism (c. 470 Ma).

### *6.3. Implications for future studies on I- and S-type granites*

The objective of carrying out this study was that S-type granites are believed to be produced by melting of crustal sedimentary rocks, and therefore provide the opportunity to study one of the end-members commonly contributing to I-type granites. Thus, three granites that show typical characteristics of S-type granites (two micas, high proportion of country rock xenoliths and inherited zircon, high  $\text{SiO}_2$  contents, peraluminous affinity etc.) were selected. To increase the likelihood of a common source the chosen granites are exposed in the same country rocks, and based on gradational contacts with their current country rocks were thought to have been generated in-situ.

However, based on this integrated oxygen, U-Pb and Hf isotope study of zircons the petrogenetic histories of the granites are not so simple. Rather than forming by melting their current country rocks the granites were probably generated at deeper levels than indicated by field relationships either by: (1) Melting and mixing of at least two supracrustal sources; in the Nigg Bay Granite one supracrustal component

represents local low- $\delta^{18}\text{O}$ , possibly hydrothermally altered material; Or (2) mixing between one or more supracrustal source(s) and a primitive infracrustal source.

To fully resolve the origin and evolution of the Kemnay, Cove and Nigg Bay granites a more extensive study is required. Nevertheless, this pilot study shows that S-type granites, like I-type granites, may have complex petrogenetic histories and may comprise multiple sources (supracrustal + infracrustal). This raises several important questions: (1) Are the Kemnay, Cove and Nigg Bay S-type granites an exception? Or do the majority of S-type granites in Scotland and worldwide have much more complex petrogenetic histories than recognised by conventional analytical methods? (2) If the low  $\delta^{18}\text{O}$  (zircon) values observed in Nigg Bay Granite represent a supracrustal rather than an infracrustal source, do I-type granites in reality comprise much larger proportions of supracrustal components, but oxygen isotopes fail to identify them?

## 6. Conclusions

- 1) Zircon  $\epsilon\text{Hf}$  values of the Kemnay, Cove and Nigg Bay granites suggest an old, probably predominantly Proterozoic-age, supracrustal precursor; no evidence was found of a contemporaneous mantle component. Comparison of zircon  $\epsilon\text{Hf}$  values with those calculated for the Dalradian Supergroup show good agreement between the granites and rocks of the Appin Group and to lesser extent with those of the Argyll Group. Furthermore, concordant  $^{207}\text{Pb}/^{206}\text{Pb}$  ages of inherited cores found in the granites match the age spectra determined on detrital zircons of the Appin, Argyll and Southern Highland groups. Based on these data the granites appear to have melted a Dalradian source and most likely exactly the same source, which is consistent with field evidence.
- 2) The Kemnay and Cove granites show mean zircon oxygen isotope compositions of 9.2 ‰ and 10.0 ‰, hence values typical of S-type granites. However, magmatic zircons of the Nigg Bay Granite have a lower mean  $\delta^{18}\text{O}$  value (7.3 ‰), similar to those found in I-type granites. Thus, at least the Nigg Bay Granite contains a different source.

- 3) Combined  $\delta^{18}\text{O}$  and  $\epsilon\text{Hf}$  data for magmatic and inherited zircon in the Kemnay, Cove and Nigg Bay granites define two near-parallel trends, which indicate mixing between at least two components in all three granites, which may be either at least two supracrustal sources, or supracrustal and infracrustal sources. This suggests that the granites did not form in-situ by melting of their current country rocks, but at deeper levels.
- 4) Large differences can be observed between the granites in the degree of zircon oxygen isotope heterogeneity. An explanation for this may be found in the different body sizes and in the degree of mixing. The Kemnay Granite, by far the largest of the three, shows the most variation, which probably results from melting and inefficient mixing of much larger, and therefore potentially isotopically more variable, volume of material. The much smaller Cove and Nigg Bay granites display considerably less variation (c. 2.5 ‰) suggesting thorough mixing during and after melting.
- 5) The Kemnay, Cove and Nigg Bay granites were emplaced at  $457 \pm 3$  Ma,  $458 \pm 5$  Ma and  $465 \pm 5$  Ma, respectively; hence they are essentially post-tectonic with respect to the peak Grampian Event deformation (D2) and metamorphism (c. 470 Ma). This observation also supports the formation of the granites at deeper crustal levels.

# **VI.**

## **CONCLUSIONS**

## Conclusions

This PhD study aimed to use the isotope and trace element record preserved in zircon crystals from granitic rocks in order to:

- Constrain the contribution made by the voluminous late Caledonian I-type granites to Phanerozoic continental growth.
- Test existing models for, and provide new insights into, granite genesis, ascent and emplacement.
- Evaluate the scales of heterogeneity, and hence the complexity of plutonic systems, by combining information obtained on a range of scales, from whole plutons to intra-crystal.
- Determine the compositions and ages of the sources of Caledonian granite suites in more detail, explaining their observed whole-rock geochemical differences, and test existing models of the nature, ages and origins of the basement underlying the Grampian terrane.
- Assess the applicability - and identify the limitations - of integrated multi-isotope and trace element studies of zircon to answering the above questions.

### **1. Applicability and limitations of integrated multi-isotope and trace element analyses of zircon**

This PhD study shows that the integration of oxygen, U-Pb and Hf isotope data from zircons is a very powerful approach to deciphering the origin and evolution of granites, while trace element/REE data from zircons have been found to be of limited use as petrogenetic indicators. On a regional scale it was possible to resolve questions regarding the sources and emplacement of the Caledonian I- and S-type granites, and the basement beneath the Grampian Highlands. On a wider scale the study makes a significant contribution to our understanding of Phanerozoic crustal growth and the complexity of plutonic systems, and provides strong evidence for recent models of magma generation and pluton assembly.

However, some limitations of this approach have also been recognised:

1. Based on oxygen isotope data alone it was not possible to constrain the proportion of contemporary mantle-derived material. Similarly in order to calculate initial Hf isotope compositions U-Pb isotope data are required. Thus, the origin and evolution of granites can only be resolved by integration of oxygen, U-Pb and Hf isotope data.
2. As analyses by ion microprobe and laser ablation ICPMS are time-consuming as well as very expensive, zircons from only a relatively small number of samples can be analysed, which raises the question whether these samples are representative of an entire pluton.
3. Even though the spatial resolution of modern ion microprobes is already very good it is not possible to analyse every growth zone within a zircon crystal, and thus to investigate its complete growth history. This is further limited by the occurrence of cracks and inclusions within the zircon crystals, which have to be avoided during analysis. Outermost zircon rims are commonly too thin to analyse, which results in an over-representation of data obtained from the zircon's central area.
4. Growth histories of individual crystals or samples may be controlled by local processes, and may not be representative of entire magma bodies.
5. In order to resolve relatively subtle variations in Hf isotope composition a laser beam size of approximately 50  $\mu\text{m}$  is required. Thus, Hf isotope data quite possibly represent a mixture of zones with differing Hf isotope composition. In addition, due to the large beam size it is often impossible to make more than one analysis per zircon crystal.
6. By analysing zircons from mineral separates the relationship to the host rock is lost. However, in thin sections the orientations of zircon crystals are ambiguous, which also makes it difficult to interpret the data in a 3-dimensional context.
7. Studies using zircon are based on the assumption that zircon crystallises early in a magma's history. However, the timing of zircon crystallisation is dependent on

a number of factors, particularly magma composition and to a lesser extent temperature, and not all of these factors are well-constrained.

## **2. The origin and sources of the Caledonian granites**

### *2.1. Crustal growth vs. crustal differentiation*

The majority of the continental crust appears to have formed between late Archaean and late Proterozoic times, perhaps intermittently during several rapid crustal growth events (Hawkesworth and Kemp, 2006a, b). However, it has recently been demonstrated that many Phanerozoic orogenic belts (e.g. Central Asian Orogenic Belt, China; Lachlan Fold Belt, southeastern Australia) also contain significant amounts of juvenile crust (DePaolo et al., 1991; Jahn et al., 2000; Samson et al., 1989; Samson et al., 1995; Wu et al., 2000); an integrated oxygen, U-Pb and Hf isotope study of zircon revealed that between 50 % and 85 % of new crust was added by at least some of the Lachlan Fold Belt 'I-type' granite plutons (Kemp et al., 2007).

Recent thermal models suggest that 'deep crustal hot zones', which develop due to repeated intrusion of mantle-derived hydrous basalt sills into the lower and/or middle crust, may play an important role in the generation of intermediate and silicic igneous rocks (Annen et al., 2006; Annen and Sparks, 2002). In these hot zones melt generation is thought to occur in three different ways: (1) by differentiation of hydrous basaltic magma, (2) by mixing between silicic melts, possibly generated by partial melting of infracrustal and/or supracrustal rocks (e.g. Druitt et al., 1999), and mantle-derived mafic magmas, and (3) by partial melting of pre-existing crustal rocks which may include early basalt sills or older mafic lower crust (Annen et al., 2006). All three models involve crustal growth to some degree. However, in model 3 the basaltic intrusions primarily act as a lower- or mid-crustal heat source and are not necessarily an important component of the resulting intermediate and silicic magmas, which thus largely represent crustal differentiation.

Previous whole-rock studies delivered inconclusive results regarding the origin and sources of the voluminous Scottish late Caledonian I-type granites. Some authors proposed that the granites comprise juvenile (mantle) and infracrustal components (Halliday et al., 1979, 1980; Harmon and Halliday, 1980; Clayburn et al., 1983; Halliday, 1984), and thus possibly played an important role in Phanerozoic crustal growth; others suggested melting of infracrustal and supracrustal sources, and thus recycling of pre-existing material (Frost and O’Nions, 1985). Based on the results of this PhD study a step has been made towards resolving this for two large plutons (the Etive and Lochnagar Plutons) representing the Argyll and Cairngorm suites respectively.

Zircon  $\delta^{18}\text{O}$  values range from  $5.3\text{-}8.1 \pm 0.6 \text{ ‰}$  (mean= $6.6 \text{ ‰}$ ,  $2\sigma$ ) in the Lochnagar and  $4.6\text{-}8.2 \pm 0.4 \text{ ‰}$  (mean= $6.5 \text{ ‰}$ ,  $2\sigma$ ) in the Etive pluton. Some zircon crystals with mantle-like compositions ( $5.3 \pm 0.6 \text{ ‰}$  ( $2\sigma$ , Valley et al., 1998)) occur within the plutons, but the majority (~80 %) display oxygen isotope compositions that are more  $^{18}\text{O}$ -enriched than pristine mantle values. Based on these data a model of magma generation by simple differentiation of basaltic material (model 1) can be ruled out. As the oxygen isotope composition of zircon is insensitive to differentiation (Valley et al., 1994) a much larger proportion of zircons with mantle-like  $\delta^{18}\text{O}$  values would be expected. Thus, the plutons were either generated by mixing between silicic partial melts and mantle-derived mafic magmas (model 2) or by remelting and recycling of pre-existing crustal rocks (model 3). From oxygen isotope data alone it is impossible to distinguish between contributions made by contemporary mantle-derived material and by old mafic lower crust, thus between models 2 and 3. However, the combination of oxygen and Hf isotope data is a powerful method to resolve this important question. Zircons from the Lochnagar pluton display  $\epsilon\text{Hf}$  values of +3.4 to -5.8, and those of the Etive pluton display a less radiogenic range of -3.0 to -10.6, whereas by comparison  $\epsilon\text{Hf}$  of depleted mantle at 420 Ma is ~ +16. In addition, Hf model ages calculated for the plutons are considerably older than their zircon U-Pb crystallisation ages as follows: Lochnagar: U-Pb = 424-413 Ma,  $\text{TDM}_\text{C}$  ~ 1.7-1.1 Ga,  $\text{TDM}_\text{W}$  ~ 1.4-1.0 Ga; Etive: U-Pb = 423-407 Ma,  $\text{TDM}_\text{C}$  ~ 2.1-1.3 Ga,  $\text{TDM}_\text{W}$  ~ 1.8-1.2 Ga (where  $\text{TDM}_\text{C}$  is calculated based on the  $^{176}\text{Lu}/^{177}\text{Hf}$  ratio of the average crust and  $\text{TDM}_\text{W}$  on the  $^{176}\text{Lu}/^{177}\text{Hf}$  ratio of



each whole-rock sample). Hence, a significant contribution by melts derived from contemporary depleted mantle can be excluded.

Little is known about the composition of the mantle beneath the Grampian terrane, but it has been suggested that the mantle below Scotland is highly heterogeneous and at least locally enriched (Canning et al., 1998; Thirlwall, 1982). For the Lochnagar pluton involvement of an enriched mantle component cannot be excluded, but the much more negative  $\epsilon_{\text{Hf}}$  values of zircons from the Etive pluton make it less likely here. Thus, the integration of zircon oxygen and Hf isotope data provide strong evidence that the Lochnagar and Etive plutons, and possibly the late Caledonian I-type granites as a whole, made some contribution to continental growth, but also comprise a large recycled component (at least the Etive pluton).

## *2.2. Crustal sources of the Lochnagar and Etive plutons*

Based on their differing whole-rock geochemical compositions the Lochnagar and Etive plutons have been interpreted to belong to different granite suites – the Cairngorm and Argyll suites, respectively (Halliday et al., 1984). Using whole-rock analysis alone it was not possible to determine the origin of the differences between the suites, but it was proposed that they either reflect heterogeneities in the composition and age of the underlying lower crust and/or mantle, or differences in the relative contributions made by crust and mantle (Halliday et al., 1984).

Using zircon oxygen and Hf isotope data I have been able to demonstrate (1) that the Lochnagar and Etive plutons comprise similar amounts of mafic material, and (2) that these were predominantly sourced from the lower crust. A supracrustal contribution from Dalradian metasedimentary country rocks cannot be precluded, but given the lack of field evidence (e.g. xenoliths - pristine or partly digested - are very rare) and the plutons'  $\delta^{18}\text{O}$  (zircon) compositions of  $6.6 \pm 0.6 \text{ ‰}$  (Lochnagar) and  $6.5 \pm 0.4 \text{ ‰}$  (Etive), which are much lower than those of typical Dalradian metasediments (e.g. Anderson et al., 2004; Frost and O'Nions, 1985), may not have played an important role. Hence, the whole-rock geochemical differences between the plutons, and on a wider scale between the Cairngorm and Argyll suites, were probably predominantly inherited from their lower crustal and possibly their mantle

sources. Significant differences in the ranges of  $\epsilon_{\text{Hf}}$  values and Hf model ages between the plutons indicate that the lower crust beneath the Grampian terrane is a heterogeneous mixture of Archaean- to Neoproterozoic-age material. The contributions from these sources vary between the plutons, with the Lochnagar pluton predominantly representing larger proportions of Mesoproterozoic-age, and the Etive pluton of Palaeo- and Mesoproterozoic-age lower crust. However, as due to lack of outcrop little is known by direct observation about the basement beneath the Grampian Highlands the nature and age of the lower crustal sources currently cannot be constrained in more detail.

### *2.3. The genesis of the Caledonian Kemnay, Cove and Nigg Bay S-type granites*

Based on gradational contacts between the granites and their country rocks it has been suggested that the majority of the Scottish Caledonian S-type granites, including the Kemnay, Cove and Nigg Bay granites, were generated more or less in-situ (Kneller and Aftalion, 1987; Richardson and Powell, 1976), by melting of the host metasedimentary rocks. As the Kemnay, Cove and Nigg Bay granites are currently exposed in the same country rocks, i.e. the Aberdeen Formation of the Dalradian Supergroup, they were thought to have sourced exactly the same supracrustal material. However, as the granites vary greatly in outcrop size (Kemnay:  $\sim 36 \text{ km}^2$ ; Cove:  $\sim 1.7 \text{ km}^2$ ; Nigg Bay: even smaller than the Cove Granite), the possibility that the larger granite bodies contain material of source(s) located at deeper levels in the crust could not be discounted.

Supporting evidence for a dominant Dalradian source was found in the U-Pb ages of inherited zircons from the Kemnay, Cove and Nigg Bay granites, which occur in 60-95 % of all analysed zircon crystals and yield similar ages as those reported for detrital zircons from the Dalradian Supergroup (Cawood et al., 2003), and in the Hf isotope data of magmatic zircons, which match Hf isotope data calculated from published Nd data of the Dalradian Appin and Argyll groups. However, zircon oxygen isotope data provide strong evidence that at least the Nigg Bay Granite sourced different material than the Kemnay and Cove granites. With mean  $\delta^{18}\text{O}$  (magmatic zircon) values of 9.2 ‰ and 10.0 ‰ the Kemnay and Cove granites most

likely formed by melting of only supracrustal material including their current country rocks. The combination of zircon  $\epsilon\text{Hf}$  and  $\delta^{18}\text{O}$  indicates mixing between at least two components. In contrast, zircons from the Nigg Bay Granite are considerably less enriched in  $^{18}\text{O}$  with a mean composition of magmatic zircons of 7.3 ‰, which is similar to the oxygen isotope composition of magmatic zircons found in I-type plutons. Inherited cores display even lower values of 4.1-7.7 ‰ (mean = 5.8 ‰). Based on these data the Nigg Bay Granite formed by mixing between supracrustal, possibly Argyll ± Southern Highland Group rocks and an infracrustal source with mantle-like oxygen and crustal Hf isotope characteristics. Alternatively, the low  $\delta^{18}\text{O}$  values observed in the Nigg Bay Granite were produced by melting of a local low- $\delta^{18}\text{O}$ , possibly hydrothermally altered, unit within the Appin or Argyll groups. Differences in the degree of mixing resulted in a large spread in  $\delta^{18}\text{O}$  in zircons from the Kemnay Granite, and tight data clusters in the Cove and Nigg Bay Granites.

This study shows that all three S-type granites comprise at least two different source components and did not form in-situ by simple melting of their current country rocks, which suggests that S-type granites, like I-type granites, have much more complicated petrogenetic histories than previously recognised. The low  $\delta^{18}\text{O}$  values found in magmatic and inherited zircons from the Nigg Bay Granite suggest that either (1) the granite is not a true S-type granite, but a mixture of I- and S-type, or (2) Dalradian metasediments comprise at least locally relatively large amounts of low- $\delta^{18}\text{O}$  material, which raises the question if the late Caledonian I-type granites perhaps contain a larger proportion of Dalradian supracrustal material than previously recognised.

### **3. Complexities of plutonic systems**

Based on detailed mapping of plutons of the Inyo Batholith, and outlier of the Sierra Nevada batholith in California, Krauskopf (1968) in his paper “A Tale of Ten Plutons” suggested that plutons are extremely complex systems that are generated in the lower crust or the upper mantle from where they ascend, subdivide, differentiate, and mingle in an apparently random manner that fundamentally limits our ability to

rationalise, describe and quantify an unambiguous intrusive history from field and geochemical data. Thus, what may appear to be a single pluton or a phase within a pluton based on criteria such as proximity between outcrops, petrography (mineralogy and texture), abundance of dykes and/or enclaves and contact metamorphic effects, may actually comprise several individual magma batches derived from different sources, with differing petrogenetic histories and even of different ages. This raises the question of the extent to which geological maps really capture the identity and petrogenetic history of plutons, and on a wider scale how meaningful tectonic or crustal evolution models that are based on geological maps or a small number of whole-rock samples are.

Strong evidence for this complexity has been provided by recent studies using information stored in zircon. The most significant contributions to our understanding of the origin and evolution of granites have been made by e.g. Kemp et al. (2007), who integrated zircon oxygen, U-Pb and Hf isotope data of zircons from Lachlan Fold Belt I-type granites to demonstrate that the assumed I-type plutons actually comprise a mixture of mantle-derived juvenile and supracrustal sources, and by Coleman et al. (2004), who used ultra-high precision U-Pb data of granitic rocks of the Tuolumne Intrusive suite (Sierra Nevada) to show that the suite was emplaced over a period of c. 10 m.y., and thus comprises magma batches of differing age that were assembled incrementally.

This PhD study makes a major contribution to our understanding of the scale, nature and complexity of plutons. In the Lochnagar and Etive plutons some of this complexity and also differences in complexity between plutons were recognised at outcrop scale. The Lochnagar pluton has previously been mapped as a simple composite pluton comprising two main granite facies (L1 and L2), a third, locally developed, granite facies (L3), microgranites and several marginal diorites (Oldershaw, 1974; Smith et al., 2001). All phases are at outcrop scale relatively homogeneous and may be distinguished by their mineralogical and textural characteristics. In contrast, the Etive pluton comprises four main intrusive phases (the Meall Odhar, Cruachan, Starav and Quarry intrusions), which range in composition from granite to monzodiorite/diorite (Batchelor, 1987; Clayburn et al., 1983). In particular the Cruachan and Quarry intrusions comprise numerous variants

that differ in grain size, major and accessory phase assemblage (Batchelor, 1987; Stephenson et al., 1999).

Oxygen isotope data of zircons from the Lochnagar and Etive plutons are actually very similar between the plutons. Zircons from the Lochnagar pluton cover a range between 5.3 ‰ and  $8.1 \pm 0.6$  ‰ with a mean of  $6.6 \pm 0.6$  ‰ ( $2\sigma$ ,  $n=230$ ); zircons from the Etive pluton spread between  $4.6-8.2 \pm 0.4$  ‰ with a mean of  $6.5 \pm 0.4$  ‰ ( $2\sigma$ ,  $n=209$ ). Thus, in both plutons the data spread is considerably larger than the analytical uncertainty, which suggests that real variation in oxygen isotope compositions occurs in zircons on a pluton scale. Evidence for this heterogeneity was found when comparing  $\delta^{18}\text{O}$  values of samples collected within separate mapped units, but also from within a single mapped unit. In the Lochnagar pluton the two samples collected from within the Allt Darrarie diorite differ in their mean oxygen isotope composition and also in their data distribution with zircons from sample AD1 showing a mean  $\delta^{18}\text{O}$  value of  $7.1 \pm 0.4$  ( $2\sigma$ ,  $n=42$ ) and an apparent bimodal distribution, and those from AD2 having a mean composition of  $6.6 \pm 0.5$  ( $2\sigma$ ,  $n=32$ ) and a unimodal distribution. The same variation can be observed between zircons from three L2 granite samples. In the Etive pluton the most variation occurs between zircons from four different samples collected in the Cruachan Intrusion. Zircons from two of these samples (Cr-11 & Cr-17) are very heterogeneous (range up to 3 ‰) and randomly distributed, whereas those of the other two (Cr-15 & Cr-26) are relatively homogeneous and show a unimodal distribution. Thus, samples from both the Lochnagar and Etive plutons may be homogeneous or heterogeneous in their distribution of zircon  $\delta^{18}\text{O}$  values. Heterogeneous samples appear to be more abundant in the Etive pluton (6 out of 10 are heterogeneous) in comparison to the Lochnagar pluton (2 out of 10 are heterogeneous). In heterogeneous samples of both plutons, resolvable variations in  $\delta^{18}\text{O}$  occur between zircon crystals and within zircon crystals of a single sample. Where resolvable intra-grain variations were detected, both decreases and increases of  $\delta^{18}\text{O}$  with zircon growth were observed, providing evidence for magma mixing.

U-Pb isotope data reveal that the emplacement histories of both plutons are more protracted and complicated than previously recognised with magmatic activity at the Lochnagar pluton lasting for c. 11 m.y. ( $424 \pm 5$  Ma to  $413 \pm 4$  Ma) and at the Etive

pluton for c. 16 m.y. ( $423 \pm 2$  Ma and  $407 \pm 2$  Ma). Even individual mapped units like the Allt Darrarie diorite (Lochnagar) or the Cruachan Intrusion (Etive) appear to have been emplaced in multiple magma batches rather than in a single pulse (Allt Darrarie diorite: AD1 =  $419 \pm 2$  Ma, AD2 =  $413 \pm 4$  Ma; Cruachan Intrusion: Cr-11 =  $421 \pm 5$  Ma, Cr-17 =  $414 \pm 6$  Ma, Cr-15 =  $413 \pm 6$  Ma, Cr-26 =  $413 \pm 4$  Ma). This provides strong support for recent models of granite emplacement, which suggest that many (and possibly the majority) of plutons are assembled incrementally as a series of sheet-like intrusions over time spans an order of magnitude longer than the thermal lifetime of large magmatic masses, and never existed as a large molten magma body (Brown and McClelland, 2000; Coleman et al., 1995; Wiebe, 1993; Wiebe and Collins, 1998).

These new data suggest that many plutons may be isotopically heterogeneous at all geological scales, raising important questions about the suitability of traditional sampling strategies, and about where the direction, emphasis and scale(s) of interest of future petrogenetic studies of granitic plutons should lie. On the one hand, the new zircon data of this PhD study and of previous studies support Krauskopf's (1968) view about the complexity of granites and the difficulties of mapping granitoid intrusions. They certainly explain why field and whole-rock studies have often delivered inconclusive results or were not able to resolve the petrogenetic evolution of granites. On the other hand, although Krauskopf (1968) doubted that even high-precision geochemical data would be able to resolve the origin and evolution of granites, by carrying out these detailed micro-analytical studies using zircon it has been possible to set much tighter and more quantitative constraints on granite sources, genesis, evolution and emplacement mechanisms, and therefore on the role granites play in the generation and differentiation of the continental crust.

# **VII.**

## **FUTURE WORK**

## Future Work

This PhD project has resolved many regional as well as wider-scale ‘granite’ questions, and has provided a number of ideas for future studies:

- One of the major outcomes of this project is that the Etive pluton and possibly also the Lochnagar pluton made at most a small contribution to continental growth. Further work, involving similar studies of other plutons, is now required to determine the extent to which these two large plutons are representative of the late Caledonian I-type suites.
- Minor appinitic and lamprophyric intrusions, which are broadly contemporaneous with the I-type plutons, have been reported from numerous locations in the Grampian Highlands (Stephenson et al., 1999 and references therein). In addition, evidence mainly in the form of mafic facies and enclaves for the involvement of contemporaneous (~430-400 Ma) basic mantle-derived magma has been found in some of the Argyll (Strontian, Ratagain, Glen Scaddle, Rogart, Ross of Mull plutons) and South Grampians suite (Glen Tilt, Garabal Hill-Glen Fyne, Glen Doll, Comrie plutons) I-type plutons (Stephenson et al., 1999), which suggests that contemporaneous mantle-derived magmas contributed at least locally to the I-type plutons. In order to place quantitative constraints on the amount of mantle input and to obtain more information on the composition of the mantle beneath the Grampian Highlands it is important to carry out integrated oxygen, U-Pb and Hf isotope studies on zircons from plutons thought to comprise contemporaneous (~430-400 Ma) mafic material, and on selected appinites and lamprophyres. At the same time, a thorough investigation of the age and origin of mafic enclaves in Caledonian granite plutons is required to establish their genetic (cognate) or accidental relationship with the host granites.
- Emplacement ages of juvenile igneous rocks exposed in different parts of the world show peaks at 2.7, 1.9 and 1.2 Ga (Condie, 1998; McCulloch and Bennett, 1994), which has led to the interpretation that much of the continental crust was generated in pulses of relatively rapid growth rather than continuously. This has been confirmed by integrated oxygen, U-Pb and Hf isotope studies of inherited



zircons from Lachlan Fold Belt I- and S-type plutons and detrital zircons of the surrounding Ordovician-age metasedimentary rocks (Hawkesworth and Kemp, 2006a, b; Kemp et al., 2006), which showed that crustal generation in Gondwana probably occurred in two major pulses at 3.3 Ga and 1.9 Ga. A study of major granitic plutonism during these periods of rapid crustal growth using the new methodologies used in this and other very recent studies is now required to characterise the nature, age and processes of periods of rapid crustal growth in more detail and to compare the results for those of this study, where crustal growth as represented by the Caledonian I-type granites appears to have been limited.

- In order to further constrain the complexities of plutonic systems and the scales of heterogeneity of various geochemical signatures, an integrated oxygen, U-Pb and Hf isotope study of zircons on samples from a small area (e.g. 100 x 100 m, or 1 x 1 km) within a single mapped unit of a pluton should be carried out in combination with documentation of field/outcrop scale heterogeneity. On the same samples further independent evidence should be sought for petrological, mineralogical, geochemical and isotopic heterogeneities indicative of multiple magma sources and magma mixing; a detailed CL imaging, and geochemical (e.g. Ginibre et al., 2007 and references therein) and isotopic study of plagioclases (e.g. Davidson et al., 2007 and references therein) in granites and diorites in which isotopic evidence for heterogeneity has been recognised in this study would be an obvious starting point for such studies. For example, the Allt Darrarie diorite of the Lochnagar pluton would be very suitable, as it has already been demonstrated in this PhD study that it comprises at least two magma batches of differing composition and age.
- In order to reach the precision necessary to resolve subtle changes in zircon  $\delta^{18}\text{O}$  with zircon growth a beam size of  $\sim 20\text{ }\mu\text{m}$  is required on the Cameca ims-1270 ion microprobe, which makes it impossible to analyse the complete growth history of a zircon crystal. Recent work by Page et al. (2007) has demonstrated that the Cameca ims-1280 ion microprobe can achieve precisions of 0.3 ‰ (2SD) on 10  $\mu\text{m}$  spots. Even though this spatial resolution still does not permit analysing every growth zone in a zircon crystal it possibly allows making double

the number of analyses. An interesting exercise would be to use the Cameca ims-1280 ion microprobe to analyse some of the zircon crystals from this PhD that show oxygen isotope variation in order to gain further insight into intra-grain scale heterogeneities.

- It has been demonstrated in this project that zircons may contain a cryptic record of magma mixing. No other petrological evidence for magma mixing has been found in either the Lochnagar or Etive plutons. For future work it would be interesting to employ the integrated oxygen, U-Pb and Hf isotope approach on zircons from a pluton known to have experienced extensive magma mixing. A good target would be the Irish late Caledonian Galway Granite, where good evidence for magma mixing has been observed in studies based on field and whole-rock data over several decades.
- To fully resolve the origin and evolution of the Caledonian Kemnay, Cove and Nigg Bay S-type granites, and the extent to which these are representative of the ~475-460 Ma S-type granites of the Scottish Caledonides, a more extensive study is required on a more comprehensive sample suite. Such a study should include detailed mapping of the granites and their country rocks, collection of a much larger number of samples (of the granites, country rock xenoliths and the country rocks), whole-rock oxygen isotope analysis of all samples, and additional oxygen, U-Pb and Hf isotope analysis of zircons.

# **VIII.**

## **REFERENCES**

## References

- Amelin, Y., Lee, D.-C., Halliday, A.N., Pidgeon, R.T., 1999. Nature of the Earth's earliest crust from hafnium isotopes in single detrital zircons. *Nature*, 399: 252-255.
- Anders, E., Grevesse, N., 1989. Abundances of the elements: Meteoritic and solar. *Geochimica et Cosmochimica Acta*, 53: 197-214.
- Andersen, T., Griffin, W.L. 2004. Lu-Hf and U-Pb isotope systematics of zircons from the Storgangen intrusion, Rogaland Intrusive Complex, SW Norway: implications for the composition and evolution of Precambrian lower crust in the Baltic Shield. *Lithos*, 73: 271-288.
- Andersen, T., Griffin, W.L., Pearson, N.J., 2002. Crustal evolution in the SW part of the Baltic Shield: the Hf isotope evidence. *Journal of Petrology*, 43: 1725-1747.
- Anderson, R., Graham, C.M., Boyce, A.J., Fallick, A.E., 2004. Metamorphic and basin fluids in quartz-carbonate-sulphide veins in the SW Scottish Highlands: a stable isotope and fluid inclusion study. *Geofluids*, 4: 169-185.
- Annen, C., Blundy, J.D., Sparks, R.S.J., 2006. The genesis of intermediate and silicic magmas in deep crustal hot zones. *Journal of Petrology*, 47: 505-539.
- Annen, C., Sparks, R.S.J., 2002. Effects of repetitive emplacement of basaltic intrusions on thermal evolution and melt generation in the crust. *Earth and Planetary Science Letters*, 203: 937-955.
- Atherton, M.P., Ghani, A.A., 2002. Slab breakoff: a model for Caledonian, Late Granite syn-collisional magmatism in the orthotectonic (metamorphic) zone of Scotland and Donegal, Ireland. *Lithos*, 62: 65-85.
- Atherton, M.P., Petford, N., 1993. Generation of sodium-rich magmas from newly underplated basaltic crust. *Nature*, 362: 144-146.
- Bailey, E.B., Maufe, A.B., 1960. The Geology of Ben Nevis and Glen Coe. Memoir of the Geological Survey, Sheet 53, 2nd edition.
- Baker, D.R., Conte, A.M., Freda, C., Ottolini, L., 2002. The effect of halogens on Zr diffusion and zircon dissolution in hydrous metaluminous granitic melts. *Contributions to Mineralogy and Petrology*, 142: 666-678.
- Barber, A.J., May, F., 1975. The history of the Lewisian in the Glenelg Attadale Inlier, lochalsh, Northern Highlands. *Scottish Journal of Geology*, 12: 35-50.
- Batchelor, R.A., 1987. Geochemical and petrological characteristics of the Etive granitoid complex, Argyll. *Scottish Journal of Geology*, 23: 227-249.
- Bateman, P.C., Chappell, B.W., 1979. Crystallization, fractionation, and solidification of the Tuolumne intrusive series, Yosemite National Park, California. *Geological Society of America Bulletin*, 90: 465-482.

- Bea, F. 1996. Residence of REE, Y, Th and U in granites and crustal protoliths; implications for the chemistry of crustal melts. *Journal of Petrology*, 37: 521-552.
- Bell, K., 1968. Age relations and provenance of the Dalradian series of Scotland. *Geological Society of America Bulletin*, 79: 1167-1194.
- Belousova, E.A., Griffin, W.L., O'Reilly, S.Y., Fisher, N.I., 2002. Igneous zircon: trace element composition as an indicator of source rock type. *Chemical Geology*, 143: 602-622.
- Belousova, E.A., Griffin, W.L., Pearson, N.J., 1998. Trace element composition and cathodoluminescence properties of southern African Kimberlite zircons. *Mineralogical Magazine*, 62: 355-366.
- Benisek, A., Finger, F., 1993. Factors controlling the development of prism faces in granite zircons. *Contributions to Mineralogy and Petrology*, 114: 441-451.
- Bindeman, I.N., Valley, J.W., 2001. Low  $\delta^{18}\text{O}$  rhyolites from Yellowstone: Magmatic evolution based on analysis of zircons and individual phenocrysts. *Journal of Petrology*, 42: 1491-1517.
- Black, L.P., Williams, I.S., Compston, W., 1986. Four zircon ages from one rock: the history of a 3930 Ma-old granulite from Mount Sones, Enderby Land, Antarctica. *Contributions to Mineralogy and Petrology*, 94: 427-437.
- Blichert-Toft, J., Albarède, F., 1997. The Lu-Hf isotope geochemistry of chondrites and the evolution of the mantle-crust system. *Earth and Planetary Science Letters*, 148: 243-258.
- Bluck, B.J., 1983. Role of the Midland Valley of Scotland in the Caledonian orogeny. *Transaction of the Royal Society of Edinburgh, Earth Sciences*, 74: 119-136.
- Bluck, B.J., 1984. Pre-Carboniferous history of the Midland Valley of Scotland. *Transaction of the Royal Society of Edinburgh, Earth Sciences*, 75: 279-295.
- Bons, P.D., Arnold, J., Elburg, M.A., Kalda, J., Soesoo, A., van Milligen, B.P., 2004. Melt extraction and accumulation from partially molten rocks. *Lithos*, 78: 25-42.
- Booth, A.L., Kolodny, Y., Chamberlain, C.P., McWilliams, M., Schmitt, A.K., Wooden, J., 2005. Oxygen isotopic composition and U-Pb discordance in zircon. *Geochimica et Cosmochimica Acta*, 69: 4895-4905.
- Brewer, T.S., Storey, C.D., Parrish, R.R., Temperley, S., Windley, B.F., 2003. Grenvillian age exhumation of eclogites in the Glenelg-Attadale Inlier, NW Scotland. *Journal of the Geological Society, London*, 160: 565-574.
- Brown, E.H., McClelland, W.C., 2000. Pluton emplacement by sheeting and vertical ballooning in part of the Southeast Coast plutonic complex, British Columbia. *Geological Society of America Bulletin*, 112: 708-719.

- Brown, G.C., Francis, E.H., Kennan, P. Stillman, C.J., 1985. Caledonian igneous rocks of Britain and Ireland. In: A.L. Harris (Editor), *The Nature and Timing of Orogenic Activity in the Caledonian Rocks of the British Isles* Geological Society, London, pp. 1-15.
- Brown, G.C., Locke, C.A., 1979. Space-time variations in British Caledonian granites: some geophysical correlations. *Earth and Planetary Science Letters*, 45: 69-79.
- Brown, J.F., 1975. Rb-Sr studies and related chemistry on the Caledonian calc-alkaline igneous rocks of NW Argyllshire, University of Oxford, Oxford.
- Brown, P.E., 1991. Caledonian and earlier magmatism. In: Craig, G.Y. (Editor), *Geology of Scotland* (3rd edition). Geological Society, London, pp. 229-295.
- Brown, P.E., Miller, J.A., Grasty, R.L., 1968. Isotopic ages of late Caledonian granitic intrusions in the British Isles. *Proceedings of the Yorkshire geological Society*, 36: 251-276.
- Buddington, A.F., 1959. Granite emplacement with special reference to North America. *Geological Society of America Bulletin*, 70: 671-747.
- Canning, J.C., Henney, P.J., Morrison, M.A., van Calsteren, P.W.C., Gaskarth, J.W., Swarbrick, A., 1998. The Great Glen Fault: a major vertical lithospheric boundary. *Journal of the Geological Society*, London, 155: 425-428.
- Cavosie, A.J., Valley, J.W., Wilde, S.A., E.I.M.F., 2005. Magmatic  $\delta^{18}\text{O}$  in 4400-3900 Ma detrital zircons: A record of the alteration and recycling of the crust in the Early Archean. *Earth and Planetary Science Letters*, 235: 663-681.
- Cawood, P.A., Nemchin, A.A., Smith, M., Loewy, S., 2003. Source of the Dalradian Supergroup constrained by U-Pb dating of detrital zircon and implications for the East Laurentian margin. *Journal of the Geological Society*, London, 160: 231-246.
- Chappell, B.W., Stephens, W.E., 1988. Origin of infracrustal (I-type) granite magmas. *Transaction of the Royal Society of Edinburgh, Earth Sciences*, 79: 71-86.
- Chappell, B.W., White, A.J.R., 1974. Two contrasting granite types. *Pacific Geology*, 8: 173-174.
- Chappell, B.W., White, A.J.R., 2001. Two contrasting granite types: 25 years later. *Australian Journal of Earth Sciences*, 48: 827-831.
- Chappell, B.W., White, A.J.R., Williams, I.S., Wyborn, D., Wyborn, L.A.I., 2000. Lachlan Fold Belt granites revisited: high- and low-temperature granites and their implications. *Australian Journal of Earth Sciences*, 47: 123-138.
- Chappell, B.W., White, A.J.R., Wyborn, D., 1987. The importance of residual source material (restite) in granite petrogenesis. *Journal of Petrology*, 28: 1111-1138.

- Chen, Y.D., Williams, I.S., 1990. Zircon inheritance in mafic inclusions from Bega Batholith granites, southeastern Australia: an ion microprobe study. *Journal of Geophysical Research*, 95: 17787-17796.
- Claoué-Long, J.C., Compston, W., Roberts, J., Fanning, C.M., 1995. Two Carboniferous ages: a comparison of SHRIMP zircon dating with conventional zircon ages and  $^{40}\text{Ar}/^{39}\text{Ar}$  analysis. *Geochronology Time Scales and Global Stratigraphic Correlation*, SEPM Special Publication, 54: 3-21.
- Clayburn, J.A.P., 1981. Age and petrogenetic studies of some magmatic and metamorphic rocks in the Grampian Highlands, University of Oxford, Oxford.
- Clayburn, J.A.P., Harmon, R.S., Pankhurst, R.J., Brown, J.F., 1983. Sr, O, and Pb isotope evidence for origin and evolution of Etive Igneous Complex, Scotland. *Nature*, 303: 492-497.
- Clemens, J.D., Mawer, C.K., 1992. Granitic magma transport by fracture propagation. *Tectonophysics*, 204: 339-360.
- Coleman, D.S., Glazner, A.F., Miller, J.S., Bradford, K.J., Frost, T.P., Joye, J.L., Bachl, C.A., 1995. Exposure of a Late Cretaceous layered mafic-felsic magma system in the central Sierra Nevada batholith, California. *Contributions to Mineralogy and Petrology*, 120: 129-136.
- Coleman, D.S., Gray, W., Glazner, A.F., 2004. Rethinking the emplacement and evolution of zoned plutons: Geochronologic evidence for incremental assembly of the Tuolumne Intrusive Suite, California. *Geology*, 32: 433-436.
- Collins, W.J., 1996. Lachlan Fold Belt granitoids: products of three-component mixing. *Transactions of the Royal Society of Edinburgh: Earth Sciences*, 87: 171-181.
- Collins, W.J., 1998. An evaluation of petrogenetic models for Lachlan Fold Belt granitoids: implications for crustal architecture and tectonic models. *Australian Journal of Earth Sciences*, 45: 483-500.
- Collins, W.J., 1999. Evaluation of petrogenetic models for Lachlan Fold Belt granitoids: implications for crustal architecture and tectonic models - Reply. *Australian Journal of Earth Sciences*, 46: 831-836.
- Compston, W., Williams, I.S., 1984. U-Pb Geochronology of Zircons from Lunar Breccia 73217 Using a Sensitive High Mass-Resolution Ion Microprobe. *Journal of Geophysical Research*, 89: B525-B534.
- Condie, K.C., 1998. Episodic continental growth and supercontinents: a mantle avalanche connection? *Earth and Planetary Science Letters*, 163: 97-108.
- Corfu, F., Hanchar, J.M., Hoskin, P.W.O., Kinny, P., 2003. Atlas of zircon textures. In: Hanchar, J.M., Hoskin, P.W.O. (Editors), *Zircon. Reviews in Mineralogy & Geochemistry*, pp. 468-500.

- Coward, M.P., 1990. The Precambrian, Caledonian and Variscan framework to NW Europe. In: Hardman, R.F.P., Brooks, J. (Editors), *Tectonic Events Responsible for Britain's Oil and Gas Reserves*. Geological Society, London, Special Publications, pp. 1-34.
- Criss, R.E., Taylor, H.P.Jr., 1986. Meteoric-hydrothermal systems. In: Valley, J.W., Taylor, H.P.Jr., O'Neil, J.R. (Editors), *Stable isotopes in high temperature geological processes*. Mineralogical Society of America Reviews in Mineralogy, pp. 373-424.
- Dallmeyer, R.D., Strachan, R.A., Rogers, G., Watt, G.R., Friend, C.R.L., 2001. Dating deformation and cooling in the Caledonian thrust nappes of north Sutherland, Scotland: insights from  $^{40}\text{Ar}/^{39}\text{Ar}$  and Rb-Sr chronology. *Journal of the Geological Society*, London, 158: 501-512.
- Davidson, J.P., Morgan, D.J., Charlier, L.A., 2007. Isotopic Microsampling of Magmatic Rocks. *Elements*, 3: 253-259.
- Dempster, T.J., Hudson, N.F.C., Rogers, G., 1995. Metamorphism and cooling of the NE Dalradian. *Journal of the Geological Society*, London, 152: 383-390.
- Dempster, T.J., Rogers, G., Tanner, P.W.G., Bluck, B.J., Muir, R.J., Redwood, S.D., Ireland, T.R., Paterson, B.A., 2002. Timing and deposition, orogenesis and glaciation within the Dalradian rocks of Scotland: constraints from U-Pb ages. *Journal of the Geological Society*, London, 159: 83-94.
- DePaolo, D.J., 1981. Trace-element and isotopic effects of combined wallrock assimilation and fractional crystallisation. *Earth and Planetary Science Letters*, 53: 189-202.
- DePaolo, D.J., Linn, A.M., Schubert, G., 1991. The continental crust age distribution: Methods of determining mantle separation ages from Sm-Nd isotopic data and implication to the southwestern United States. *Journal of Geophysical Research*, 96.
- Detrick, R.S., Mutter, J.C., Buhl, P., Kim, I.I., 1990. No evidence from multichannel reflection data for a crustal magma chamber in the MARK area on the Mid-Atlantic Ridge. *Nature*, 347: 61-64.
- Dewey, J.F., Mange, M., 1999. Petrology of Ordovician and Silurian sediments in the Western Irish Caledonides: tracers of a short-lived Ordovician continent-arc collision orogeny and the evolution of the Laurentian-Appalachian-Caledonian margin. In: MacNiocail, C., Ryan, P.D. (Editors), *Continental Tectonics*. Geological Society, London, Special Publications, pp. 55-108.
- Dewey, J.F., Ryan, P.D., 1990. The Ordovician evolution of the South Mayo Trough, western Ireland. *Tectonics*, 9: 887-903.
- Dewey, J.F., Shackleton, R.J., 1984. A model for the evolution of the Grampian tract in the early Caledonides and Appalachians. *Nature*, 312: 115-120.



- Dickinson, J.E., Jr., Hess, P.C., 1982. Zircon saturation in lunar basalts and granites. *Earth and Planetary Science Letters*, 57: 336-344.
- Dodson, M.H., 1973. Closure temperature in cooling geochronological and petrological systems. *Contributions to Mineralogy and Petrology*, 40: 259-274.
- Dowty, E., 1980. Crystal growth and nucleation theory and the numerical simulation of igneous crystallization In: Hargraves, R.B. (Editor), *Physics of Magmatic Processes*. Princeton University Press, Princeton, New Jersey, pp. 419-485.
- Druitt, T.H., Edwards, L., Mellors, R.M., Pyle, D.M., Sparks, R.S.J., Lanphere, M., Davies, M., Barriero, B., 1999. Santorini Volcano. *Geological Society of London, Memoirs*, 19.
- Eiler, J.M., 2001. Oxygen isotope variations of basaltic lavas and upper mantle rocks. *Reviews in Mineralogy and Geochemistry*, 43: 319-364.
- Farver, J.R., Yund, R.A., 1991. Oxygen diffusion in quartz; dependence on temperature and water fugacity. *Chemical Geology*, 90: 55-70.
- Faure, G., Mensing, T.M., 2004. *Isotopes: Principles and Applications*. Wiley, 928 pp.
- Foden, J.D., Green, D.H., 1992. Possible role of amphibole in the origin of andesite: some experimental and natural evidence. *Contributions to Mineralogy and Petrology*, 109: 479-493.
- Fowler, A., Prokoph, A., Stern, R., Dupuis, C., 2002. Organization of oscillatory zoning in zircon: Analysis, scaling, geochemistry, and model of a zircon from Kipawa, Quebec, Canada. *Geochimica et Cosmochimica Acta*, 66: 311-328.
- Fowler, M.B., Henney, P.J., Darbyshire, D.P.F., Greenwood, P.B., 2001. Petrogenesis of high Ba-Sr granites: the Rogart pluton, Sutherland. *Journal of the Geological Society, London*, 158: 521-534.
- Fraser, G.L., Pattison, D.R.M., Heamann, L.M., 2004. Age of the Ballachulish and Glencoe Igneous Complexes (Scottish Highlands), and paragenesis of zircon, monazite and baddeleyite in the Ballachulish Aureole. *Journal of the Geological Society, London*, 161: 447-462.
- Fron del, C., 1953. Hydroxyl substitution in thorite and zircon. *American Mineralogist*, 38: 1007-1018.
- Frost, C.D., Bel, J.M., Frost, B.R., Chamberlain, K.R., 2001. Crustal growth by magmatic underplating: Isotopic evidence from the northern Sherman batholith. *Geology*, 29: 515-518.
- Frost, C.D., O'Nions, R.K., 1985. Caledonian magma genesis and crustal recycling. *Journal of Petrology*, 26: 515-544.

- Frost, T.P., Mahood, G.A., 1987. Field, chemical, and physical constraints on mafic-felsic magma interaction in the Lamarck Granodiorite, Sierra Nevada, California. *Geological Society of America Bulletin*, 99: 272-291.
- Gill, J., 1981. *Orogenic Andesites and Plate Tectonics*. Springer, Berlin, 390 pp.
- Ginibre, C., Wörner, G., Kronz, A., 2007. Crystal Zoning as an Archive for Magma Evolution. *Elements*, 3: 261-266.
- Glazner, A., Bartley, J.M., Coleman, D.S., Gray, W., Taylor, R.Z., 2004. Are plutons assembled over millions of years by amalgamation from small magma chambers? *GSA today*, 14: 4-11.
- Glazner, A.F., Bartley, J.M., 2006. Is stoping a volumetrically significant pluton emplacement process? *GSA Bulletin*, 118: 1185-1195.
- Gould, D., 1997. Geology of the country around Inverurie and Alford. *Memoir of the Geological Survey, Sheets 76E and 76W (Scotland)*.
- Gray, C.M., 1984. An isotopic mixing model for the origin of granitic rocks in southeastern Australia. *Earth and Planetary Science Letters*, 70: 47-60.
- Gray, D.R., Foster, D.A., 1997. Orogenic concepts - application and definition: Lachlan Fold Belt, eastern Australia. *American Journal of Science*, 297: 859-891.
- Griffin, W.L., Belousova, E.A., Shee, S.R., Pearson, N.J., O'Reilly, S.Y., 2004. Archean crustal evolution in the northern Yilgarn Craton: U-Pb and Hf isotope evidence from detrital zircons. *Precambrian Research*, 131: 231-282.
- Griffin, W.L., Pearson, N.J., Belousova, E.A., Jackson, S.E., van Achterbergh, E., O'Reilly, S.Y., Shee, S.R., 2000. The Hf isotope composition of cratonic mantle: LAM-MC-ICPMS analysis of zircon megacrysts in kimberlites. *Geochimica et Cosmochimica Acta*, 64: 133-147.
- Griffin, W.L., Wang, X., Jackson, S.E., Pearson, N.J., O'Reilly, S.Y., Xu, X., Zhou, X., 2002. Zircon chemistry and magma mixing, SE China: In-situ analysis of Hf isotopes, Tonglu and Pingtan igneous complexes. *Lithos*, 61: 237-269.
- Gromet, L.P., Silver, L.T., 1983. Rare earth element distributions among minerals in a granodiorite and their petrogenetic implications. *Geochimica et Cosmochimica Acta*, 47: 925-939.
- Grove, T.L., Donnelly-Nolan, J.M., Housh, T., 1997. Magmatic processes that generated the rhyolite Glass Mountain, Medicine Lake volcano, N California. *Contributions to Mineralogy and Petrology*, 127: 205-223.
- Grove, T.L., Elkins-Tanton, L.T., Parman, S.W., Cjatterjee, N., Müntener, O., Gaetani, G.A., 2003. Fractional crystallisation and mantle-melting controls on calc-alkaline differentiation trends. *Contributions to Mineralogy and Petrology*, 145: 515-533.

- Grove, T.L., Kinzler, R.J., 1986. Petrogenesis of andesites. *Annual Review of Earth and Planetary Sciences*, 14: 417-454.
- Grove, T.L., Parman, S.W., Bowring, S.A., Price, R.C., Baker, M.B., 2002. The role of an H<sub>2</sub>O-rich fluid component in the generation of primitive basaltic andesites and andesites from Mt. Shasta region, N California. *Contributions to Mineralogy and Petrology*, 142: 375-396.
- Guo, J., O'Reilly, S.Y., Griffin, W.L., 1996. Zircon inclusions in corundum megacrysts: I. Trace element geochemistry and clues to the origin of corundum megacrysts in alkali basalts. *Geochimica et Cosmochimica Acta*, 60: 2347-2363.
- Halliday, A.N., 1984. Coupled Sm-Nd and U-Pb systematics in late Caledonian granites and the basement under northern Britain. *Nature*, 307: 229-233.
- Halliday, A.N., Aftalion, M., van Breemen, O., Jocelyn, J., 1979. Petrogenetic significance of Rb-Sr and U-Pb isotopic systems in the 400 Ma old British Isles granitoids and their hosts. In: Harris, A.L., Holland, C.H., Leake, B.E. (Editors), *The Caledonides of the British Isles - Reviewed*. Special Publications. Geological Society, London Special Publications, pp. 653-662.
- Halliday, A.N., Stephens, W.E., 1984. Crustal controls on the genesis of the 400 Ma old Caledonian granites. *Physics of the Earth and Planetary Interiors*, 35: 89-104.
- Halliday, A.N., Stephens, W.E., Harmon, R.S., 1980. Rb-Sr and O isotopic relationships in 3 zoned Caledonian granitic plutons, Southern Uplands, Scotland: evidence for varied sources and hybridization of magmas. *Journal of the Geological Society, London*, 137: 329-348.
- Halliday, A.N., Stephens, W.E., Hunter, R.H., Menzies, M.A., Dickin, A.P., Hamilton, P.J., 1985. Isotopic and chemical constraints on the building of the deep Scottish lithosphere. *Scottish Journal of Geology*, 21: 465-491.
- Hamilton, P.J., O'Nions, R.K., Pankhurst, R.J., 1980. Isotopic evidence for the provenance of some Caledonian granites. *Nature*, 287: 279-284.
- Hanchar, J.M., Miller, C.F., 1993. Zircon zonation patterns as revealed by cathodoluminescence and backscattered electron images: Implications for interpretation of complex crustal histories. *Chemical Geology*, 110: 1-13.
- Hanchar, J.M., Rudnick, R.L., 1995. Revealing hidden structures: The application of cathodoluminescence and backscattered electron imaging to dating zircons from lower crustal xenoliths. *Lithos*, 36: 289-303.
- Harmon, R.S., 1983. Oxygen and strontium isotope evidence regarding the role of continental crust in the origin and evolution of the British Caledonian granites. In: Atherton, M.P., Gribble, C.D. (Editors), *Migmatites, Melting and Metamorphism*. Shiva, Orpington, pp. 62-79.

- Harmon, R.S., Halliday, A.N., 1980. Oxygen and strontium isotope relationships in the British late Caledonian granites. *Nature*, 283: 21-25.
- Harris, A.L., Baldwin, C.T., Bradbury, H.J., Johnson, H.D., Smith, R.A., 1978. Ensialic basin sedimentation: the Dalradian Supergroup. In: Bowes, D.R., Leake, B.E. (Editors), *Crustal Evolution in Northwest Britain and Adjacent Regions*. Geological Journal Special Issue, pp. 115-138.
- Harris, A.L., Haselock, P.J., Kennedy, M.J., Mendum, J.R., 1994. The Dalradian Supergroup in Scotland, Shetland and Ireland. In: W. Gibbsons, Harris, A.L. (Editor), *A Revised Correlation of Precambrian Rocks in the British Isles*. Geological Society, London, Special Report, pp. 33-53.
- Harrison, T.M., Watson, E.B., Aikman, A.B., 2007. Temperature spectra of zircon crystallisation in plutonic rocks. *Geology*, 35: 635-638.
- Hawkesworth, C.J., Kemp, A.I.S., 2006a. Using hafnium and oxygen isotopes in zircons to unravel the record of crustal evolution. *Chemical Geology*, 226: 144-162.
- Hawkesworth, C.J., Kemp, A.I.S., 2006b. Evolution of the continental crust. *Nature*, 443: 811-817.
- Heaman, L.M., Bowins, R., Crocket, J., 1990. The chemical composition of igneous zircon suites: implications for geochemical tracer studies. *Geochimica et Cosmochimica Acta*, 54: 1597-1607.
- Highton, A.J., Hyslop, E.K., Noble, S.J., 1999. U-Pb geochronology of migmatisation in the Northern Central Highlands: evidence for pre-Caledonian (Neoproterozoic) tectonomorphism in the Grampian block, Scotland. *Journal of the Geological Society*, London, 156: 1195-1204.
- Hinton, R.W., Upton, B.G.J., 1991. The chemistry of zircon: variations within and between large crystals from syenite and alkali basalt xenoliths. *Geochimica et Cosmochimica Acta*, 55: 3287-3302.
- Hoffmann, C., 1981. Chi-square testing of zircon populations from an Archean granite-greenstone terrain, Minas Gerais, Brazil. *Neues Jahrbuch Mineralogische Abhandlungen*, 140: 202-220.
- Hoskin, P.W.O., 1998. Minor and trace element analysis of natural zircon (ZrSiO<sub>4</sub>) by SIMS and laser ablation ICPMS: a consideration and comparison of two broadly competitive techniques. *Journal of Trace and Microprobe Techniques*, 16: 301-326.
- Hoskin, P.W.O., Ireland, T.R., 2000. Rare earth element chemistry of zircon and its use as a provenance indicator. *Geology*, 28: 627-630.
- Hoskin, P.W.O., Schaltegger, U., 2003. The composition of zircon and igneous and metamorphic petrogenesis. In: Hanchar, J.M., Hoskin, P.W.O. (Editors), *Zircon. Reviews in Mineralogy & Geochemistry*, pp. 27-62.

- Izbekov, P., Gardner, J.E., Eichelberger, J.C., 2004. Comagmatic granophyre and dacite from Karymsky volcanic center, Kamchatka; experimental constraints and magma storage conditions. *Journal of Volcanology and Geothermal Research*, 131: 1-18.
- Iziuka, T., Hirata, T., 2005. Improvements of precision and accuracy in in situ Hf isotope microanalysis of zircon using the laser ablation-MC-ICPMS technique. *Chemical Geology*, 220: 121-137.
- Jackson, M.D., Cheadle, M.J., Atherton, M.P., 2003. Quantative modeling of granitic melt generation and segregation in the continental crust. *Journal of Geophysical Research*, 108: 2332.
- Jacques, J.M., Reavy, R.J., 1994. Caledonian plutonism and major lineaments in the SW Scottish Highlands. *Journal of the Geological Society, London*, 151: 955-969.
- Jahn, B.M., Wu, F.Y., Hong, D.W., 2000. Important crustal growth in the Phanerozoic: Isotopic evidence of granitoids from East-Central Asia. *Proceedings of the Indian Academy of Science*, 109: 5-20.
- John, B.E., Wooden J., 1990. Petrology and geochemistry of the metaluminous to peraluminous Chemehuevi Mountains Plutonic suite, northeastern California. In: Anderson, J.L. (Editor), *The Nature and Origin of Cordilleran Magmatism*. Geological Society of America, Memoir, pp. 71-98.
- John, B.E., Wooden J., 1990. Petrology and geochemistry of the metaluminous to peraluminous Chemehuevi Mountains Plutonic suite, northeastern California. In: J.L. Anderson (Editor), *The Nature and Origin of Cordilleran Magmatism*. Geological Society of America, Memoir, pp. 71-98.
- Kay, L., 1980. Oxygen and hydrogen isotope ratio study of Caledonian rocks from northeast Scotland, PhD thesis, University of Aberdeen.
- Kelemen, P.B., 1995. Genesis of high Mg# andesites and the continental crust. *Contributions to Mineralogy and Petrology*, 120: 1-19.
- Kelly N.M., Hinton, R.W., Harley, S.L., Appleby, S.K., (accepted). New SIMS U-Pb zircon ages from the Langavat Belt, South Harris, NW Scotland: implications for the Lewisian Terrane Model. Accepted at *Journal of the Geological Society, London*.
- Kemp, A.I.S., Hawkesworth, C.J., 2003. Granitic perspectives on the generation and secular evolution of the continental crust. In: Holland, H.D., Turekian, K.K. (Editors), *Treatise on Geochemistry - The Crust*. Elsevier, pp. 349-410.
- Kemp, A.I.S., Hawkesworth, C.J., Foster, G.L., Paterson, B.A., Woodhead, J.D., Hergt, J.M., Gray, C.M., Whitehouse, M.J., 2007. Magmatic and crustal differentiation history of granitic rocks from Hf-O isotopes in zircon. *Science*, 315: 980-983.

- Kemp, A.I.S., Hawkesworth, C.J., Paterson, B.A., Kinny, P.D., 2006. Episodic growth of the Gondwana supercontinent from hafnium and oxygen isotopes in zircon. *Nature*, 439: 580-583.
- Kemp, A.I.S., Wormald, R.J., Whitehouse, M.J., Price, R.C., 2005b. Hf isotopes in zircon reveal contrasting sources and crystallization histories for alkaline to peralkaline granites of Temora, southeastern Australia. *Geology*, 33: 797-800.
- Keppler, H., 1993. Influence of fluorine on the enrichment of high field strength trace elements in granitic rocks. *Contributions to Mineralogy and Petrology*, 114: 479-488.
- King, E.M., Barrie, C.T., Valley, J.W., 1997. Hydrothermal alteration of oxygen isotope ratios in quartz phenocrysts, Kidd Creek mine, Ontario: Magmatic values are preserved in zircon. *Geology*, 25: 1079-1082.
- King, E.M., Beard, B.L., Johnson, C.M., Valley, J.W., 2002. Oxygen and strontium isotopic evidence for the abrupt and steeply-dipping suture between lithospheric plates in the Idaho batholith. *Geological Society of America, Abstracts with Programs*, 34: 180.
- King, E.M., Valley, J.W., 2001. The source, magmatic contamination, and alteration of the Idaho batholith. *Contributions to Mineralogy and Petrology*, 142: 72-88.
- King, E.M., Valley, J.W., Davis, D.W., 2000. Oxygen isotope evolution of volcanic rocks at the Sturgeon Lake volcanic complex, Ontario. *Canadian Journal of Earth Science*, 37: 39-50.
- King, E.M., Valley, J.W., Davis, D.W., Edwards, G.R., 1998. Oxygen isotope ratios of Archean plutonic zircons from granite-greenstone belts of the Superior Province: indicator of magmatic source. *Precambrian Research*, 92: 365-387.
- King, E.M., Valley, J.W., Stockli, D.F., Wright, J.E., 2004. Oxygen isotope trends of granitic magmatism in the Great Basin: Location of the Precambrian craton boundary as reflected in zircons. *GSA Bulletin*, 116: 451-462.
- Kinny, P.D., Maas, R., 2003. Lu-Hf and Sm-Nd isotope systems in zircon. In: Hanchar, J.M., Hoskin, P.W.O. (Editors), *Zircon. Reviews in Mineralogy & Geochemistry*, pp. 327-341.
- Kinny, P.D., Strachan, R.A., Rogers, G.R., Friend, C.R.L., Knocks, H., 2003. U-Pb geochronology of deformed meta-granites in central Sutherland, Scotland: evidence for widespread Silurian metamorphism and ductile deformation of the Moine Supergroup during the Caledonian orogeny. *Journal of the Geological Society, London*, 160: 259-269.
- Kistler, R.W., Chappell, B.W., Peck, D.L., Bateman, P.C., 1986. Isotopic variation in the Tuolumne Intrusive Suite, central Sierra Nevada, California. *Contributions to Mineralogy and Petrology*, 94: 205-220.

- Kneller, B.C., Aftalion, M., 1987. The isotopic and structural age of the Aberdeen granite. *Journal of the Geological Society, London*, 144: 717-722.
- Köppel, V., Sommerauer, J., 1974. Trace elements and the behaviour of the U-Pb system in inherited and newly formed zircons. *Contributions to Mineralogy and Petrology*, 43: 71-82.
- Kostov, I., 1973. Zircon morphology as a crystallogenic indicator. *Kristall und Technik*, 8: 11-19.
- Krauskopf, K.B., 1968. A Tale of Ten Plutons. *Geological Society of America Bulletin*, 79: 1-18.
- Lackey, J.S., 2005. The magmatic and alteration history of the Sierra Nevada batholith as recorded by oxygen isotope ratios in zircon, titanite, garnet, and quartz. PhD thesis, University of Wisconsin.
- Lackey, J.S., Valley, J.W., Hinke, H.J., 2006. Deciphering the source and contamination history of peraluminous magmas using  $\delta^{18}\text{O}$  of accessory minerals: examples from garnet-bearing plutons of the Sierra Nevada batholith. *Contributions to Mineralogy and Petrology*, 151: 20-44.
- Lackey, J.S., Valley, J.W., Saleeby, J.B., 2005. Supracrustal input to magmas in the deep crust of Sierra Nevada batholith: Evidence from high  $\delta^{18}\text{O}$  zircon. *Earth and Planetary Science Letters*, 235: 315-330.
- Larsen, L., 1973. Measurement of solubility of zircon ( $\text{ZrSiO}_4$ ) in synthetic granitic melts. *EOS*, 54: 479.
- Larsen, L.H., Poldervaart, A., 1957. Measurement and distribution of zircons in some granitic rocks of magmatic origin. *Mineralogical Magazine*, 31: 544-564.
- Leake, B.E., 1978. Granite emplacement: the granites of Ireland and their origin. In: D.R. Bowes, Leake, B.E. (Editor), *Crustal evolution in northwestern Britain and adjacent regions*. *Journal of the Geological Society, Special Issue*, pp. 221-248.
- Linnen, R.L., Keppler, H., 2002. Melt composition control of Zr/Hf fractionation in magmatic processes. *Geochimica et Cosmochimica Acta*, 66: 3293-3301.
- Lister, C.R.B., 1983. On the intermittancy and crystallization mechanisms of sub-seafloor magma chambers. *Geophysical Journal of the Royal Astronomical Society*, 73: 351-365.
- Lister, J.R., Kerr, R.C., 1991. Fluid-mechanical models of crack propagation and their application to magma transport in dykes. *Journal of Geophysical Research*, 96: 10049-10077.
- Ludwig, K.R., 2003. Isoplot 3.00. Berkeley Geochronology Center Special Publication No. 4

- Macaulay, C.I., Fallick, A. E., Haszeldine, R. S., Graham, C. M., 2000. Methods of laser-based stable isotope measurement applied to diagenetic cements and hydrocarbon reservoir quality. *Clay Minerals*, 35: 313-322.
- Matzel, J.E.P., Bowring, S.A., Miller, R.B., 2006. Time scales of pluton construction at differing crustal levels: Examples from the Mount Stuart and Tenpeak intrusions, North Cascades, Washington. *GSA Bulletin*, 118: 1412-1430.
- Maurice, O.D., 1949. Transport and deposition of the non-sulphide vein minerals. V. Zirconium minerals. *Economic Geology*, 44: 721-731.
- May, F., Peacock, J.D., Smith, D.I., Barber, A.J., 1993. Geology of the Kintail district. Memoir of the Geological Survey, Sheet 72W and Part of 71E.
- McCulloch, M.T., Chappell, B.W., 1982. Nd isotopic characteristics of S- and I-type granites. *Earth and Planetary Science Letters*, 58: 51-64.
- McCulloch, M.T., Wasserburg, G.J., 1978. Sm-Nd and Rb-Sr chronology of continental crust formation. *Science*, 200: 1003-1011.
- Miller, C.F., Wooden, J.F., Bennett, V.C., Wright, J.E., Solomon, G.C., Hurst, R.W., 1990. Petrogenesis of the composite peraluminous-metaluminous Old Woman-Piute Range batholith, southeastern California; isotopic constraints. In: J.L. Anderson (Editor), *The Nature and Origin of Cordilleran Magmatism*. Geological Society of America, Memoir, pp. 99-109.
- Monani, S., Valley, J.W., 2001. Oxygen isotope ratios of zircon: magma genesis of low  $\delta^{18}\text{O}$  granites from the British Tertiary Igneous Province, western Scotland. *Earth and Planetary Science Letters*, 184: 377-392.
- Morris, G.A., Page, L., Martinez, V., 2005. New dates (415 Ma) for the Etive Dyke Swarm and the end of the Caledonian Orogeny in the SW Grampian Highlands of Scotland. *Journal of the Geological Society, London*, 162: 741-744.
- Mortazavi, M., Sparks, R.S.J., 2004. Origin of rhyolite and rhyodacite lavas and associated mafic inclusions of Cape Akrotiri, Santorini: the role of wet basalt in generating calcalkaline silicic magmas. *Contributions to Mineralogy and Petrology*, 146: 397-413.
- Muir, R.J., 1990. The Precambrian basement and related rocks of the southern Inner Hebrides, Scotland, University of Wales, Aberystwyth.
- Muir, R.J., Fitches, W.R., Maltman, A.J., 1994b. The Rhinns Complex: Proterozoic basement on Islay and Colonsay, Inner Hebrides, Scotland, and on Inishtrahull, NW Ireland. *Transactions of the Royal Society of Edinburgh: Earth Sciences*, 85: 77-90.
- Munro, M., 1986. Geology of the country around Aberdeen. Memoir of the British Geological Survey, Sheet 77 (Scotland): 124.
- Müntener, O., Kelemen, P.B., Grove, T.L., 2001. The role of H<sub>2</sub>O during crystallisation of primitive arc magmas under uppermost mantle conditions and genesis of igneous



- pyroxenites: an experimental study. *Contributions to Mineralogy and Petrology*, 141: 643-658.
- Murthy, M.V.N., 1958. On the crystallization of accessory zircon in granitic rocks of magmatic origin. *Canadian Mineralogist*, 6: 260-263.
- Musselwhite, D.S., De Paolo, D.J., McCurry, M., 1989. The evolution of a silicic magma system - isotopic and chemical evidence from the Woods Mountain Volcanic Center, Eastern California. *Contributions to Mineralogy and Petrology*, 101: 19-29.
- Nebel, O., Nebel-Jacobsen, Y., Mezger, K., Berndt, J., 2007. Initial Hf isotope compositions in magmatic zircon from early Proterozoic rocks from the Gawler Craton, Australia: A test for zircon model ages. *Chemical Geology*, 241: 23-37.
- Nowell, G.M., Kempton, P.D., Noble, S.R., Fitton, J.G., Saunders, A.D., Mahoney, J.J., Taylor, R.N., 1998. High precision Hf isotope measurements of MORB and OIB by thermal ionization mass spectrometry: insights into the depleted mantle. *Chemical Geology*, 149: 211-233.
- Nowell, G.M., Pearson, D.G., Bell, D.R., Carlson, R.W., Smith, C.B., Kempton, P.D., Noble, S.R., 2004. Hf isotope systematics of kimberlites and their megacrysts: new constraints on their source regions. *Journal of Petrology*, 45: 1583-1612.
- Oldershaw, W., 1974. The Lochnagar granitic ring complex, Aberdeenshire. *Scottish Journal of Geology*, 10: 297-309.
- Oliver, G.J.H., 2001. Reconstruction of the Grampian episode in Scotland: its place in the Caledonian Orogeny. *Tectonophysics*, 332: 23-49.
- Oliver, G.J.H., Chen, F., Buchwald, R., Heger, E., 2000. Fast tectonothermal metamorphism and exhumation in the type area of the Barrovian and Buchan zones. *Geology*, 28: 459-462.
- O'Nions, R.K., Hamilton, P.J., Hooker, P.J., 1983. A Nd isotope investigation of sediments related to crustal development in the British Isles. *Earth and Planetary Science Letters*, 63: 229-240.
- Page, F.Z., Ushikubo, T., Kita, N., Riciputi, L.R., Valley, J.W., 2007. High-precision oxygen isotope analysis of picogram samples reveals 2  $\mu\text{m}$  gradients and slow diffusion in zircon. *American Mineralogist*, 92: 1772-1775.
- Pankhurst, R.J., 1974. Rb-Sr whole-rock chronology of Caledonian events in northeast Scotland. *Bulletin of the Geological Society of America*, 85: 345-350.
- Pankhurst, R.J., 1979. Isotope and trace element evidence for the origin and evolution of Caledonide granites in the Scottish Highlands. In: M.P. Atherton, Tarney, J. (Editor), *The Origin of Granite Batholiths: Geochemical Evidence*. Shiva Publishing Ltd., Kent, pp. 18-33.

- Pankhurst, R.J., Sutherland, D.S., 1982. Caledonian granites and diorites of Scotland and Ireland. In: D.S. Sutherland (Editor), *Igneous Rocks of the British Isles* Wiley, Chichester, pp. 141-190.
- Park, R.G., 1991. The Lewisian Complex. In: G.Y. Craig (Editor), *Geology of Scotland*. Geological Society of London, London, pp. 25-58.
- Park, R.G., Stewart, A.D. Wright, D.T., 2002. The Hebridean terrane. In: N.H. Trewin (Editor), *The Geology of Scotland*. The Geological Society, London, pp. 45-80.
- Patchett, P.J., Kouvo, O., Hedge, C.E., Tatsumo, M., 1981. Evolution of continental crust and mantle heterogeneity: evidence from Hf isotopes. *Contributions to Mineralogy and Petrology*, 78: 279-297.
- Paterson, S.R., Fowler, T.K., Jr., Miller, R.B., 1996. Pluton emplacement in arcs; a crustal-scale exchange process. In: M. Brown, Piccoli, P.M. (Editor), *The Third Hutton Symposium on the origin of granites and related rocks: The Geological Society of America Special Paper*, pp. 115-123.
- Peck, W.H., Valley, J.W., Graham, C.M., 2003. Slow oxygen diffusion rates in igneous zircons from metamorphic rocks. *American Mineralogist*, 88: 1003-1014.
- Peck, W.H., Valley, J.W., Wilde, S.A., Graham, C.M., 2001. Oxygen isotope ratios and rare earth elements in 3.3 to 4.4 Ga zircons: Ion microprobe evidence for high  $\delta^{18}\text{O}$  continental crust and oceans in the Early Archaean. *Geochimica et Cosmochimica Acta*, 65: 4215-4229.
- Petford, N., Atherton, M., 1996. Na-rich partial melts from newly underplated basaltic crust: the Cordillera Blanca Batholith, Peru. *Journal of Petrology*, 37: 1491-1521.
- Petford, N., Cruden, A.R., McCaffrey, K.J.W., Vigneresse, J.-L., 2000. Granite magma formation, transport and emplacement in the Earth's crust. *Nature*, 408: 669-673.
- Piasecki, M.A.J., 1980. New light on the Moine rocks of the Central Highlands of Scotland. *Journal of the Geological Society, London*, 137: 47-59.
- Pichavant, M., Martel, C., Bourdier, J.L., Scaillet, B., 2002. Physical conditions, structure, and dynamics of a zoned magma chamber: Mount Pelé (Martinique, Lesser Antilles Arc). *Journal of Geophysical Research*, 107.
- Pichavant, M., Montel, J.-M., Richard, L.R., 1992. Apatite solubility in peraluminous liquids: experimental data and an extension of the Harrison-Watson model. *Geochimica et Cosmochimica Acta*, 56: 3855-3861.
- Pickering, K.T., Bassett, M.G., Siveter, D.J., 1988. Late Ordovician-Early Silurian destruction of the Iapetus Ocean: Newfoundland, British Isles and Scandinavia - a discussion. *Transactions of the Royal Society of Edinburgh: Earth Sciences*, 79: 361-382.
- Pidgeon, R.T., Aftalion, M., 1978. Cogenetic and inherited zircon U-Pb systems in granites: Palaeozoic granites of Scotland and England. In: D.R. Bowes, Leake, B.E.

- (Editor), Crustal evolution in northwestern Britain and adjacent regions. Geological Journal Special Issues, pp. 183-220.
- Pidgeon, R.T., Compston, W., 1992. A SHRIMP ion microprobe study of inherited and magmatic zircons from four Scottish Caledonian granites. Transactions of the Royal Society of Edinburgh: Earth Sciences, 83: 473-483.
- Pitcher, W.S., Berger, A.R., 1972. The Geology of Donegal: A Study of Granite Emplacement and Unroofing. Wiley, Interscience, New York.
- Poldervaart, A., 1955. Zircons in rocks, 1. Sedimentary rocks. American Journal of Science, 235: 433-461.
- Poldervaart, A., 1956. Zircons in rocks, 2. Igneous rocks. American Journal of Science, 254: 521-554.
- Prouteau, G., Scaillet, B., 2003. Experimental constraints on the origin of the 1991 Pinatubo dacite. Journal of Petrology, 44: 2203-2241.
- Pupin, J.P., 1980. Zircon and granite petrology. Contributions to Mineralogy and Petrology, 73: 207-220.
- Pupin, J.P., Turco, G., 1972a. Une typologie originale du zircon accessoire. Bulletin Société Française de Minéralogie et de Cristallographie, 95: 348-359.
- Pupin, J.P., Turco, G., 1972b. Application des données morphologiques du zircon accessoire en pétrologie endogène. Comptes Rendus de l'Académie des Sciences Paris, 275D: 799-802.
- Pupin, J.P., Turco, G., 1972c. Le zircon accessoire en géothermométrie. Comptes Rendus de l'Académie des Sciences Paris, 274D: 2121-2124.
- Raia, F., Spera, F.J., 1997. Simulation of the growth and differentiation of continental crust. Journal of Geophysical Research, 102: 22629-22648.
- Rapp, R.P., Watson, E.B., 1995. Dehydration melting of metabasalt at 8-32 kbar - implications for continental growth and crust-mantle recycling. Journal of Petrology, 36: 891-931.
- Read, H.H., 1961. Aspects of the Caledonian magmatism in Scotland. Proceedings of the Liverpool and Manchester Geological Society, 2: 653-683.
- Reid, M.R., Coath, C.D., Harrison, T.M., McKeegan, K.D., 1997. Prolonged residence times for the youngest rhyolites associated with Long Valley Caldera:  $^{230}\text{Th}$ - $^{238}\text{U}$  ion microprobe dating of young zircons. Earth and Planetary Science Letters, 150: 27-39.
- Restrepo-Pace, P.A., Ruiz, J., Gehrels, G., Cosca, M., 1997. Geochronology and Nd isotopic data of Grenville-age rocks in the Colombian Andes: new constraints for Late Proterozoic-Early Paleozoic paleocontinental reconstructions of the Americas. Earth and Planetary Science Letters, 150: 427-441.

- Richardson, S.W., Powell, R., 1976. Thermal causes of the Dalradian metamorphism in the Central Highlands of Scotland. *Scottish Journal of Geology*, 12: 237-268.
- Rogers, G., Dunning, G.R., 1991. Geochronology of appinitic and related granitic magmatism in the W. Highlands of Scotland: constraints on the timing of transcurrent fault movement *Journal of the Geological Society, London*, 148: 17-27.
- Rogers, G., Hawkesworth, C.J., 1989. A geochemical traverse across the North Cilean Andes - evidence for crust generation from the mantle wedge. *Earth and Planetary Science Letters*, 91: 271-285.
- Rollin, R.E., 1994. Geophysical correlation of Precambrian rocks in northern Britain. In: W. Gibbons, Harris, A.L. (Editor), *A Revised Correlation of Precambrian Rocks in the British Isles*. Geological Society, London, Special Report, pp. 65-74.
- Rudnick, R.L., Fountain, D.M., 1995. Nature and composition of the continental crust: a lower crustal perspective. *Reviews in Geophysics*, 33: 267-309.
- Samson, S.D., Hibbard, J.P., Wortman, G.L., 1995. Nd isotopic evidence for juvenile crust in the Carolina terrane, southern Appalachians *Contributions to Mineralogy and Petrology*, 121: 171-184.
- Samson, S.D., McClelland, W.C., Patchett, P.J., Gehreless, G.E., Anderson, R.G., 1989. Evidence from neodymium isotopes from mantle contributions to Phanerozoic crustal genesis in the Canadian Cordillera. *Nature*, 337: 705-709.
- Sanders, I.S., van Calsteren, P.W.C., Hawkesworth, C.J., 1984. A Grenville Sm-Nd age for the Glenelg eclogite in northwest Scotland. *Nature*, 312: 439-440.
- Sano, Y., Terado, K., Fukuoka, T., 2002. High mass resolution ion microprobe analysis of rare earth elements in silicate glass, apatite and zircon: lack of matrix dependency. *Chemical Geology*, 184: 217-230.
- Scherer, E., Münker, C., Mezger, K., 2001. Calibration of the Lutetium-Hafnium Clock. *Science*, 293: 683-687.
- Scherer, E., Whitehouse, M.J., Münker, C., 2007. Zircon as a Monitor of Crustal Growth. *Elements*, 3: 19-24.
- Schuhmacher, M., de Chambost, E., McKeegan, K.D., Harrison, T.M. & Migeon, H. 1994. In-situ dating of zircon with the CAMECA ims-1270. In: *Secondary Ion Mass Spectrometry, SIMS IX* (eds. A. Benninghoven et al.), pp. 919-922. Wiley.
- Sharp, Z.D., 1990. A laser-based microanalytical method for the in situ determination of oxygen isotope ratios of silicates and oxides. *Geochimica et Cosmochimica Acta*, 54: 1353-1357.
- Shore, M., Fowler, A.D., 1996. Oscillatory zoning in minerals: a common phenomenon. *Canadian Mineralogist*, 34: 1111-1126.

- Siedner, G., 1965. Geochemical features of a strongly fractionated alkali igneous suite. *Geochimica et Cosmochimica Acta*, 29: 113-137.
- Simpson, P.R., Brown, G.C., Plant, J., Ostle, D., 1979. Uranium mineralization and granite magmatism in the British isles. *Philosophical Transactions of the Royal Society of London*, A291: 385-412.
- Sisson, T.W., Grove, T.L., 1993. Experimental investigations of the role of H<sub>2</sub>O in calc-alkaline differentiation and subduction zone magmatism. *Contributions to Mineralogy and Petrology*, 113: 143-166.
- Sisson, T.W., Moore, J.G., 1994. Geologic map of the Giant Forest Quadrangle, Tulare County, California. In: U.S.G. Survey (Editor).
- Smith, B.M., 1981. Oxygen and strontium isotopic studies of the Skye intrusive complex, Northwest Scotland, Brown University.
- Smith, C.G., Goodman, S., Robertson, S., 2001. Geology of the Ballater district. British Geological Survey - Memoir for 1:50 000 Geological Sheet 65E (Scotland).
- Smith, D.R., Leeman, W.P., 1987. Petrogenesis of Mount St. Helens dacitic magmas. *Journal of Geophysical Research*, 92: 10313-10334.
- Soper, N.J., 1986. The Newer Granite problem: a geotectonic view. *Geological Magazine*, 123: 227-236.
- Soper, N.J., Hutton, D.H.W., 1984. Late Caledonian sinistral displacements in Britain: Implications for a three-plate model. *Tectonics*, 3: 187-190.
- Soper, N.J., Ryan, P.D., Dewey, J.F., 1999. Age of the Grampian orogeny in Scotland and Ireland. *Journal of the Geological Society of London*, 156: 1231-1236.
- Soper, N.J., Strachan, R.A., Holdsworth, R.E., Gayer, R.A., Greiling, R.O., 1992. Sinistral transpression and the Silurian closure of Iapetus. *Journal of the Geological Society, London*, 149: 697-700.
- Speer, J.A., 1982. Zircon. *Reviews in Mineralogy*, pp. 67-112.
- Stephens, W.E., 1988. Granitoid plutonism in the Caledonian orogen of Europe. In: A.L. Harris, Fettes, D.J. (Editor), *The Caledonian-Appalachian Orogen*. Special Publications. Geological Society, London, pp. 389-403.
- Stephens, W.E., Halliday, A.N., 1984. Geochemical contrasts between late Caledonian granitoid plutons of northern, central and southern Scotland. *Transactions of the Royal Society of Edinburgh: Earth Sciences*, 75: 259-273.
- Stephenson, D., Gould, D., 1995. *The Grampian Highlands*. British Regional Geology. HMSO, London.
- Stephenson, D.B., R.E., Millward, D., Highton, A.J., Parsons, I., Stone, P., Wadsworth, W.J., 1999. Caledonian igneous rocks of Great Britain. *Geological Conservation Review Series*, 17. Joint Nature Conservation Committee, 1-648 pp.

- Stewart, M., Strachan, R.A., Martin, M.W. Holdsworth, R.E., 2001. Dating early sinistral displacements along the Great Glen Fault Zone, Scotland: structural setting, emplacement and U-Pb geochronology of the syn-tectonic Clunes Tonalite. *Journal of the Geological Society, London*, 158: 821-830.
- Strachan, R.A., Smith, M., Harris, A.L., Fettes, D.J., 2002. The Northern Highland and Grampian terranes. In: N.H. Trewin (Editor), *The Geology of Scotland*. The Geological Society, London, pp. 81-148.
- Sun, S.S., McDonough, W.F., 1989. Chemical and isotopic systematics of oceanic basalts: implications for mantle compositions and processes. *Geological Society, London, Special Publications*, 42: 313-345.
- Tarney, J., Jones, C.E., 1994. Trace element geochemistry of orogenic igneous rocks and crustal growth models. *Journal of the Geological Society, London*, 151: 855-868.
- Taylor, B.E., Huston, D.L., 1998. Hydrothermal alteration of oxygen isotope ratios in quartz phenocrysts, Kidd Creek mine, Ontario: Magmatic values preserved in zircons. *Geology*: 763-764.
- Technology, N.I.o.S., 1992. Reference Materials 8543-8546.
- Tepper, J.H., Nelson, B.K., Bergantz, G.W., Irving, A.J., 1993. Petrology of the Chilwack batholith, North Cascades, Washington. Generation of calc-alkaline granitoids by melting of mafic lower crust with variable water fugacity. *Contributions to Mineralogy and Petrology*, 113: 333-351.
- Thirlwall, M.F., 1981. Implications for Caledonian plate tectonic models of chemical data from volcanic rocks of the British Old Red Sandstone *Journal of the Geological Society, London*, 138: 123-138.
- Thirlwall, M.F., 1982. Systematic variation in chemistry and Nd-Sr isotopes across a Caledonian calc alkaline volcanic arc: implications for source materials. *Earth and Planetary Science Letters*, 58: 27-50.
- Thirlwall, M.F., 1988. Geochronology of Late Caledonian Magmatism in northern Britain. *Journal of the Geological Society, London*, 145: 951-967.
- Thirlwall, M.F., Walder, A.J., 1995. In situ hafnium isotope ratio analysis of zircon by inductively coupled plasma mass spectrometry. *Chemical Geology*, 122: 241-247.
- Tindle, A.G., Pearce, A., 1981. Petrogenetic modelling of in situ fractional crystallization in the zoned Loch Doon Pluton, Scotland. *Contributions to Mineralogy and Petrology*, 78: 196-207.
- Valley, J.W., 2003. Oxygen isotopes in zircon. *Reviews in Mineralogy & Geochemistry*, 53: 343-385.
- Valley, J.W., Bindemann, I.N., Peck, W.H., 2003. Empirical calibration of oxygen isotope fractionation in zircon. *Geochimica et Cosmochimica Acta*, 67: 3257-3266.

- Valley, J.W., Chiarenzelli, J.R., McLelland, J.M., 1994. Oxygen isotope geochemistry of zircon. *Earth and Planetary Science Letters*, 126: 187-206.
- Valley, J.W., Graham, C., 1996. Ion microprobe analysis of oxygen isotope ratios in quartz from Skye granite: healed micro-cracks, fluid flow, and hydrothermal exchange. *Contributions to Mineralogy and Petrology*, 124: 225-234.
- Valley, J.W., Kinny, P.D., Schulze, D.J., Spicuzza, M.J., 1998. Zircon megacrysts from kimberlite: oxygen isotope variability among mantle melts. *Contributions to Mineralogy and Petrology*, 133: 1-11.
- Valley, J.W., Kinny, P.D., Schulze, D.J., Spicuzza, M.J., 1998. Zircon megacrysts from kimberlite: oxygen isotope variability among mantle melts. *Contributions to Mineralogy and Petrology*, 133: 1-11.
- Vavra, G., 1990. On the kinematics of zircon growth and its petrogenetic significance: a cathodoluminescence study. *Contributions to Mineralogy and Petrology*, 106: 90-99.
- Vavra, G., 1993. A guide to quantitative morphology of accessory zircon. *Chemical Geology*, 110: 15-28.
- Vavra, G., 1994. Systematics of internal zircon morphology in major Variscan granitoid types. *Contributions to Mineralogy and Petrology*, 117: 331-344.
- Vernon, R.H., 1983. Restite, xenoliths and microgranitoid enclaves in granites. *Journal of the Proceedings of the Royal Society of New South Wales*, 116: 77-103.
- Vervoort, J.D., Blichert-Toft, J., 1999. Evolution of the depleted mantle: Hf isotope evidence from juvenile rocks through time. *Geochimica et Cosmochimica Acta*, 63: 533-556.
- Vervoort, J.D., Patchett, J.P., Albarede, F., Blichert-Toft, J., Rudnick, R., Downes, H., 2000. Hf-Nd isotopic evolution of the lower crust. *Earth and Planetary Science Letters*, 181: 115-129.
- Vervoort, J.D., Patchett, P.J., 1996. Behaviour of hafnium and neodymium isotopes in the crust: Constraints from Precambrian crustally derived granites. *Geochimica et Cosmochimica Acta*, 60: 3717-3733.
- Wall, V.J., Clems, J.D., Clarke, D.B., 1987. Models for granitoid evolution and source compositions. *Journal of Geology*, 95: 731-749.
- Watson, B.E., 1979. Zircon saturation in felsic liquids: Experimental results and applications to trace element geochemistry. *Contributions to Mineralogy and Petrology*, 70: 407-419.
- Watson, B.E., 1996. Dissolution, growth and survival of zircons during crustal fusion: kinetic principles, geological models and implications for isotopic inheritance. *Transactions of the Royal Society of Edinburgh: Earth Sciences*, 87: 43-56.

- Watson, B.E., Harrison, T.M., 1983. Zircon saturation revisited: temperature and composition effects in a variety of crustal magma types. *Earth and Planetary Science Letters*, 64: 295-304.
- Watson, E.B., Cherniak, D.J., 1997. Oxygen diffusion in zircon. *Earth and Planetary Science Letters*, 148: 527-544.
- Watson, E.B., Harrison, T.M., 2005. Zircon Thermometer Reveals Minimum Melting Conditions on Earliest Earth. *Science*, 308: 841-844.
- Watson, E.B., Wark, D.A., Thomas, J.B., 2006. Crystallization thermometers for zircon and rutile. *Contributions to Mineralogy and Petrology*, 151: 413-433.
- Whitehouse, M.J., Claesson, S., Sunde, T. & Vestin, J. 1997. Ion microprobe U-Pb geochronology and correlation of Archaean gneisses from the Lewisian Complex of Gruinard Bay, northwestern Scotland. *Geochimica Cosmochimica et Acta*, 61, 4429-4438.
- Wiebe, R.A., 1993. The Pleasant Bay layered gabbro-diorite, coastal maine; ponding and crystallisation of basaltic injections into a silicic magma chamber. *Journal of Petrology*, 34: 461-489.
- Wiebe, R.A., Collins, W.J., 1998. Depositional features and stratigraphic sections in granitic plutons; implications for the emplacement and crystallization of granitic magma. *Journal of Structural Geology*, 20: 1273-1289.
- Wiedenbeck, M., Alle, P., Corfu, F., Griffin, W.L., Meier, M., Oberli, F., Von Quadt, A., Roddick, J.C. & Spiegel, W. 1995. Three natural zircon standards for U-Th-Pb, Lu-Hf, trace element and REE analyses. *Geostandards Newsletter*, 19, 1-23.
- Wiedenbeck, M., Hanchar, J.M., Peck, W.H., Sylvester, P., Valley, J., Whitehouse, M., Kronz, A., Morishita, Y., Nasdala, L., Fiebig, J., Franchi, I., Girard, J.-P., Greenwood, R.C., Hinton, R., Kita, N., Mason, P.R.D., Norman, M., Ogasawara, M., Piccoli, P.M., Rhede, D., Satoh, H., Schulz-Dobrick, B., Skår, Ø., Spicuzza, M.J., Terada, K., Tindle, A., Togashi, S., Vennemann, T., Xie, Q., Zheng, Y.-F., 2004. Further Characterization of the 91500 Zircon Crystal. *Geostandards and Geoanalytical Research*, 28: 9-39.
- Williams, I.S. 1998. U-Th-Pb geochronology by ion microprobe. In: (Eds. McKibben, M.A., Shanks, W.C., & Ridley, W.I.) *Applications of Microanalytical Techniques to Understanding Mineralizing Processes*, Socorro, New Mexico, *Reviews in Economic Geology*, Society of Economic Geologists, 7, 1-35.
- Williams, I.S. & Claesson, S. 1987. Isotopic evidence for the Precambrian provenance and Caledonian metamorphism of high-grade paragneisses from the Seve Nappes, Scandinavian Caledonides: 2. Ion microprobe zircon U-Th-Pb. *Contributions to Mineralogy and Petrology*, 97, 205-217.



- Woodhead, J.D., Hergt, J.M., 2005. A preliminary appraisal of seven natural zircon reference materials for in situ Hf isotope determination. *Geostandards and Geoanalytical Research*, 29: 183-195.
- Wu, F.-Y., Jahn, B.-M., Wilde, S., Sun, D.-Y., 2000. Phanerozoic crustal growth: U-Pb and Sr-Nd isotopic evidence from the granites in northeastern China. *Tectonophysics*, 328: 89-113.
- Zaleski, E., 1983. The geology of Strathspey and Lower Findhorn granitoids - a study involving field relations, petrography, mineralogy, geochemistry and geochronology University of St. Andrews.

# **IX.**

## **APPENDICES**

# **APPENDIX 1**

## **Supplementary data for Paper 1**

Appendix 1a

Zircon oxygen isotope data for CnG (SA04/13) and AD1 (SA04/01) diorites and average values of bracketing zircon standards

analyses no.	grain no.	$^{18}\text{O}/^{16}\text{O}$ (measured)	2SD	1 s.e.m.	$\delta^{18}\text{O}$ [‰] VSMOW	2SD	1 s.e.m.	n	grain area	comment
<u>Session 4 (01.06.2005)</u>										
91500 - 11-20		0.0020157	0.0000010	0.0000002	9.78	0.5	0.075	10		
91500 - 21-30		0.0020159	0.0000008	0.0000001	9.89	0.4	0.067	10		
91500 - 36-45		0.0020160	0.0000007	0.0000001	9.92	0.3	0.051	10		
SA04/01-1	1	0.0020100			6.9				c2a	
SA04/01-2	1	0.0020109			7.4				c2b	rejected, crack
SA04/01-3	2	0.0020085			6.2				rim	rejected, crack
SA04/01-4	2	0.0020089			6.4				c2	rejected, crack
SA04/01-5	3	0.0020103			7.1				c2	
SA04/01-6	3	0.0020094			6.6				c1	
<u>Session 5 (01.06.2005)</u>										
91500 - 46-50		0.0020148	0.0000004	0.0000001	9.92	0.22	0.049	5		
SA04/01-7	4	0.0020095			7.3				?	
SA04/01-8	4	0.0020097			7.4				?	
SA04/01-9	4	0.0020095			7.3				?	
SA04/01-10	4	0.0020103			7.7				?	
SA04/01-11	5	0.0020100			7.5				rim	
SA04/01-12	5	0.0020098			7.4				c1b	
SA04/01-13	5	0.0020092			7.1				c1a	rejected, crack
SA04/01-14	6	0.0020096			7.3				c2a	
SA04/01-15	6	0.0020094			7.3				c2b	
SA04/01-16	7	0.0020092			7.2				c1a	
91500 - 51-55		0.0020145	0.0000010	0.0000002	9.76	0.48	0.107	5		
91500 - 67-70		0.0020148	0.0000012	0.0000003	9.91	0.61	0.152	4		
SA04/01-17	7	0.0020100			7.5				c1b	
SA04/01-18	7	0.0020101			7.6				rim a	
SA04/01-19	7	0.0020099			7.5				rim b	
SA04/01-20	8	0.0020085			6.8				c1	
SA04/01-22	8	0.0020086			6.9				c2a	
SA04/01-23	8	0.0020095			7.3				c2b	
SA04/01-24	8	0.0020092			7.1				c2c	
SA04/01-25	8	0.0020100			7.5				m1	
SA04/01-26	8	0.0020069			6.0				rim	rejected, overlaps epoxy
SA04/01-27	9	0.0020080			6.5				c1	rejected, correction on position of secondary ion beam anomalously large
91500 - 71-75		0.0020147	0.0000008	0.0000002	9.86	0.38	0.084	5		
SA04/01-28	9	0.0020078			6.5				c2a	
SA04/01-29	9	0.0020094			7.3				c2b	
SA04/01-30	10	0.0020095			7.3				rim	rejected, correction on position of secondary ion beam anomalously large
SA04/01-31	10	0.0020081			6.6				c2	
SA04/01-32	10	0.0020106			7.8				c1	
SA04/01-33	11	0.0020112			8.1				rim	
SA04/01-34	11	0.0020094			7.2				c1	
SA04/01-35	12	0.0020098			7.5				c2	
SA04/01-36	12	0.0020096			7.3				c1b	
SA04/01-37	12	0.0020108			8.0				c1c	rejected, convoluted, possibly altered area

Session 6 (01.06.2005)

91500 - 76-80		0.0020156	0.0000006	0.0000001	9.90	0.31	0.070	5		
SA04/01-38	12	0.0020101			7.2				c1d	rejected, crack
SA04/01-39	12	0.0020105			7.4				c1a	
SA04/01-40	12	0.0020110			7.6				c2b	rejected, crack
SA04/01-41	13	0.0020080			6.2				c2a	
SA04/01-42	13	0.0020090			6.6				c2b	
SA04/01-43	14	0.0020094			6.8				c1	
SA04/01-44	14	0.0020090			6.6				c2a	
SA04/01-45	14	0.0020097			7.0				c2b	
SA04/01-46	15	0.0020092			6.7				c1	
SA04/01-47	15	0.0020097			7.0				c3	
91500 - 81-85		0.0020154	0.0000007	0.0000002	9.81	0.32	0.081	4		
SA04/01-48	15	0.0020094			6.8				c2b	
SA04/01-49	15	0.0020090			6.6				c2a	
SA04/01-50	16	0.0020080			6.1				m1	
SA04/01-51	16	0.0020085			6.4				c1	
SA04/01-52	16	0.0020067			6.5				rim	

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91500 - 140-149		0.0020149	0.0000010	0.0000002	9.96	0.49	0.078	10		
91500 - 150-154		0.0020148	0.0000007	0.0000002	9.88	0.35	0.078	5		
91500 - 155-159		0.0020145	0.0000007	0.0000002	9.77	0.34	0.075	5		
SA04/13-1	1	0.0020093			7.2				c2a	rejected, analytical problem
SA04/13-2	1	0.0020048			4.9				c2b	rejected, analytical problem
SA04/13-3	2	0.0020077			6.4				c2b	
SA04/13-4	2	0.0020067			5.9				c2a	
SA04/13-5	2	0.0020071			6.1				c1	
SA04/13-6	3	0.0020067			5.9				c2	
91500 - 161-164		0.0020148	0.0000013	0.0000003	9.89	0.64	0.16	4		
SA04/13-7	4	0.0020061			5.6				rim	
SA04/13-8	4	0.0020076			6.3				c1a	
SA04/13-9	5	0.0020066			5.9				c2	
SA04/13-10	5	0.0020074			6.2				c1	
SA04/13-11	5	0.0020068			5.9				rim	
SA04/13-12	6	0.0020066			5.8				c1a	
SA04/13-13	6	0.0020051			5.1				c1b	rejected, crack
SA04/13-14	6	0.0020071			6.1				rim	
SA04/13-15	7	0.0020075			6.3				c1a	
SA04/13-16	7	0.0020069			6.0				m1	
SA04/13-17	7	0.0020068			5.9				c1b	
SA04/13-18	8	0.0020068			5.9				rim	
SA04/13-19	8	0.0020067			5.9				m1c	
SA04/13-20	8	0.0020064			5.8				m1b	
SA04/13-21	8	0.0020083			6.7				m1a	rejected, crack
SA04/13-22	8	0.0020065			5.8				c1	
SA04/13-24	9	0.0020066			5.8				c1	
SA04/13-25	9	0.0020071			6.1				rim	
SA04/13-26	10	0.0020059			5.5				c2	rejected, correction on position of secondary ion beam anomalously large
91500 - 170-174		0.0020147	0.0000008	0.0000002	9.87	0.40	0.09	5		
SA04/13-27	10	0.0020072			6.1				c1	rejected, correction on position of secondary ion beam anomalously large
SA04/13-28	11	0.0020073			6.2				c1	
SA04/13-29	12	0.0020066			5.8				rim	
SA04/13-30	12	0.0020059			5.5				c1	
SA04/13-31	13	0.0020064			5.7				c1	
SA04/13-32	13	0.0020063			5.7				c2	
SA04/13-33	13	0.0020064			5.8				rim	
SA04/13-34	14	0.0020060			5.5				c2	
SA04/13-35	15	0.0020061			5.6				c1	
SA04/13-36	15	0.0020073			6.2				rim	
91500 - 175-179		0.0020145	0.0000017	0.0000004	9.74	0.87	0.19	5		

SA04/13-37	16	0.0020066		5.8		c1	
SA04/13-38	17	0.0020077		6.4		c1a	
SA04/13-39	17	0.0020077		6.4		c1b	
SA04/13-40	17	0.0020076		6.3		c2	
SA04/13-41	18	0.0020069		6.0		c2a	rejected, crack
SA04/13-42	18	0.0020063		5.7		c2b	rejected, crack
SA04/13-43	18	0.0020073		6.2		rim	
SA04/13-44	19	0.0020076		6.3		c1	
SA04/13-45	19	0.0020067		5.9		rim	
SA04/13-46	3	0.0020080		6.5		c2c	rejected, crack

91500 - 175-179      0.0020146    0.0000013    0.0000003    9.80    0.66    0.17    4

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c1 = unzoned inner core  
c2 = oscillatory zoned outer core  
m1-3 = mantle

Appendix 1b  
Quartz oxygen isotope data for CnG (SA04/13) and AD1 (SA04/01) diorites and average values of bracketing quartz standard NBS28

analyses no.	grain no.	$^{18}\text{O}/^{16}\text{O}$ (measured)	2SD	1 s.e.m.	$^{18}\text{O}/^{16}\text{O}$ (drift corrected)	$\delta^{18}\text{O}$ [‰] VSMOW	2SD	1 s.e.m.	n	grain area	comment
Session 1 (29.05.2007)											
	NBS28 - 20-29	0.0020087	0.0000026	0.0000004	0.0020087	9.87	1.3	0.221	9		
	NBS28 - 30-39	0.0020085	0.0000008	0.0000001	0.0020086	9.76	0.4	0.061	10		
SA04/13	Q13/1-1	0.0020110				11.1				centre	
SA04/13	Q13/1-2	0.0020113				11.2				rim	
SA04/13	Q13/2-1	0.0020108				10.9				centre	
SA04/13	Q13/2-2	0.0020128				12.0				rim	rejected, spot in altered area
SA04/13	Q13/2-3	0.0020107				10.9				rim	
SA04/13	Q13/3c-1	0.0020106				10.9				centre	
SA04/13	Q13/3c-2	0.0020106				10.9				rim	
SA04/13	Q13/4-1	0.0020103				10.7				centre	
SA04/13	Q13/4-2	0.0020104				10.8				centre	
SA04/13	Q13/4-3	0.0020106				10.9				rim	
SA04/13	Q13/9-4	0.0020097				10.5				towards rim	
SA04/13	Q13/9-5	0.0020097				10.4				towards rim	
	NBS28 - 40-49	0.0020080	0.0000024	0.0000004	0.0020085	9.62	1.2	0.189	10		
SA04/13	Q13/9-1	0.0020107				11.0				centre	
SA04/13	Q13/9-2	0.0020108				11.0				centre	
SA04/13	Q13/7-1	0.0020101				10.7				centre	
SA04/13	Q13/7-2	0.0020106				11.0				towards rim	
SA04/13	Q13/7-3	0.0020116				11.4				rim	
SA04/13	Q13/10-1	0.0020098				10.6				centre	
SA04/13	Q13/10-2	0.0020105				10.9				towards rim	
SA04/13	Q13/15-1	0.0020116				11.4				centre	
SA04/13	Q13/15-2	0.0020110				11.2				rim	
SA04/13	Q13/14-1	0.0020109				11.1				centre	
SA04/13	Q13/14-3	0.0020110				11.2				rim	
average						10.9	0.5	0.057	22		
	NBS28 - 50-59	0.0020093	0.0000022	0.0000003	0.0020083	10.36	1.1	0.172	10		
SA04/01	Q01/1a-1	0.0020119				11.7				centre	
SA04/01	Q01/1a-2	0.0020127				12.1				towards rim	
SA04/01	Q01/1a-3	0.0020127				12.1				rim	
SA04/01	Q01/1c-1	0.0020128				12.1				centre	
SA04/01	Q01/1c-3	0.0020115				11.5				rim	
SA04/01	Q01/1c-2	0.0020124				12.0				rim	
SA04/01	Q01/2-1	0.0020116				11.5				centre	
SA04/01	Q01/2-2	0.0020119				11.7				centre	
SA04/01	Q01/2-3	0.0020110				11.3				rim	
SA04/01	Q01/3-1	0.0020111				11.3				centre	
SA04/01	Q01/3-2	0.0020117				11.6				rim	
SA04/01	Q01/4-1	0.0020126				12.1				centre	
SA04/01	Q01/4-2	0.0020129				12.2				towards rim	
SA04/01	Q01/4-3	0.0020124				12.0				rim	
SA04/01	Q01/6-1	0.0020122				11.9				centre	
SA04/01	Q01/6-2	0.0020118				11.7				rim	
	NBS28 - 60-69	0.0020082	0.0000017	0.0000003	0.0020081	9.88	0.8	0.132	10		
SA04/01	Q01/7-1	0.0020116				11.6				centre	
SA04/01	Q01/7-2	0.0020117				11.7				rim	
SA04/01	Q01/7-3	0.0020129				12.3				rim	
SA04/01	Q01/8-1	0.0020119				11.8				centre	
SA04/01	Q01/8-2	0.0020113				11.5				towards rim	
SA04/01	Q01/8-3	0.0020108				11.3				centre	
SA04/01	Q01/10-1	0.0020110				11.3				centre	
SA04/01	Q01/10-2	0.0020116				11.6				rim	
SA04/01	Q01/13-1	0.0020112				11.5				rim	
SA04/01	Q01/13-2	0.0020113				11.5				rim	
SA04/01	Q01/16-1	0.0020116				11.7				centre	
average						11.7	0.6	0.057	27		
	NBS28 - 70-79	0.0020075	0.0000023	0.0000004	0.0020079	9.66	1.1	0.180	10		

## **APPENDIX 2**

### **Supplementary data for Paper 2**



Appendix 2a

## Major, trace and rare earth element whole-rock data of the Lochnagar and Etive plutons

	Lochnagar									Etive									
	AD1 SA0401	AD2 SA0402	CnG SA0413	L1-03 SA0403	L1-06 SA0406	L2-04 SA0404	L2-15 SA0415	L2-12 SA0412	L3 SA0405	MO SA0520	Cr-11 SA0511	Cr-17 SA0517	Cr-15 SA0515	Cr-26 SA0526	Si-05 SA0505	Si-06 SA0506	Si-01 SA0501	Q-23 SA0523	Q-25 SA0525
SiO <sub>2</sub> [%]	53.0	57.5	54.6	71.8	76.11	71.59	72.9	75.0	68.8	71.8	57.1	68.44	61.53	62.22	71.9		76.1	61.4	57.2
TiO <sub>2</sub>	2.06	1.26	1.22	0.35	0.142	0.307	0.29	0.18	0.45	0.35	1.14	0.514	0.882	0.647	0.36		0.14	0.77	1.01
Al <sub>2</sub> O <sub>3</sub>	17.82	16.51	17.40	14.02	12.24	14.44	13.94	13.40	15.95	14.72	17.59	14.89	18.73	18.48	13.75		12.58	15.73	14.11
Fe <sub>2</sub> O <sub>3</sub>	9.47	6.65	7.27	1.92	0.92	1.76	1.71	1.06	2.22	1.58	6.06	3.15	4.06	2.98	2.19		0.83	5.17	7.32
MnO	0.12	0.12	0.12	0.04	0.01	0.04	0.03	0.03	0.05	0.04	0.07	0.05	0.06	0.04	0.04		0.03	0.08	0.11
MgO	3.69	4.13	4.90	0.46	0.04	0.5	0.48	0.04	0.48	0.18	2.57	1.69	1.26	0.72	0.73		0.11	3.36	6.15
CaO	6.39	5.80	7.76	1.22	0.35	1.3	1.08	0.34	1.15	0.65	5.46	2.58	3.52	2.46	1.39		0.44	4.60	6.08
Na <sub>2</sub> O	3.93	3.41	3.50	3.25	3.19	3.74	3.71	3.64	4.56	4.67	3.90	3.76	5.56	4.94	3.81		3.53	3.94	3.06
K <sub>2</sub> O	1.96	2.69	1.65	5.56	5.174	4.457	4.33	5.52	4.73	5.16	2.61	3.886	2.749	4.857	4.13		4.84	3.04	2.12
P <sub>2</sub> O <sub>5</sub>	0.64	0.22	0.23	0.05	-0.005	0.059	0.06	0.06	0.06	0.02	0.32	0.119	0.185	0.112	0.11		0.00	0.24	0.38
LOI	1.11	1.40	0.93	0.52	0.42	0.76	0.77	0.41	0.74	0.49	0.96	0.78	0.79	0.65	0.68		0.39	0.90	1.42
Sum	100.15	99.68	99.56	99.18	98.60	98.95	99.33	99.59	99.20	99.61	97.75	99.86	99.33	98.11	99.12		99.02	99.22	98.97
Sc [ppm]	25		26	4		4	4	3	4	5	18	8	1	4	4	6	3	13	23
V	176	137	153	16		18	19	7	7	6	125	46	59	26	24	40	3	92	132
Cr		24	33			1					29	36		8		19		85	191
Ni		6	33								18	9				3		44	82
Ba	870	984	547	864	309	635	523	776	1708	1421	1036	1064	1281	5917	857	1061	192	1104	662
Rb	58	78	43	123	158	165	171	143	141	106	88	101	79	71	125	97	169	69	53
Sr	831	583	775	262	70	268	229	84	325	171	1138	536	911	863	392	625	96	978	981
Y*	27	21	17	16	12	13	11	12	12	15	13	12	7	9	9	11	7	11	16
U*	1	2	1	4	4	6	8	3	2	3	3	3	2	2	4	3	10	2	2
Th*	4	3	4	16	18	17	19	18	19	12	8	12	8	11	11	12	15	6	6
Pb	10	11	8	21	26	28	29	27	25	26	13	18	16	22	22	19	34	14	12
U	427	179	230	191	93	144	146	147	339	290	124	144	623	457	140	153	70	121	143
Nb	17	10	13	18	15	16	18	16	18	16	11	11	11	8	13	13	20	10	8
Cu	18	28	31	5	4	10	11	5	5	6	28	8	11	7	7	12	10	17	36
Zn	103	74	79	32	23	39	39	28	50	41	76	46	45	43	42	50	19	65	88
La	39		27	51			30		63	43	31						18	27	
Ce	85		54	90			57		109	77	62						31	53	
Pr	11		6	9			6		10	9	7						3	6	
Nd	44		26	30			21		34	31	30						10	24	
Sm	8		5	5			3		4	5	5						1	4	
Eu	1		2	1			0		2	1	1						0	1	
Tb	3		1	1			0		0	1	1						0	0	
Gd	8		4	4			3		3	4	4						1	3	
Dy	6		4	3			2		2	3	3						1	2	
Ho	1		1	1			0		0	1	1						0	1	
Er	3		2	2			1		1	2	1						1	1	
Tm	0		0	0			0		0	0	0						0	0	
Yb	3		2	2			1		1	1	1						1	1	
Lu	0		0	0			0		0	0	0						0	0	
Hf	7		5	5			4		8	6	3						3	3	
R1	1385	1789	1792	2271	2700	2346	2477	2380	1792	2914	2368	3035	2411	2228	3250		3505	2611	2584
R2	1216	1149	1415	428	280	447	413	301	460	316	924	562	705	577	392		257	833	1047
A/CNK	0.9	0.9	0.8	1.0	1.1	1.1	1.1	1.1	1.1	1.0	0.9	1.0	1.0	1.0	1.0		1.1	0.9	0.8
A/NK	2.1	1.9	2.3	1.2	1.1	1.3	1.3	1.1	1.3	1.1	1.9	1.4	1.5	1.4	1.3		1.1	1.6	1.9
grid	NO 31780	NO 31781	NO 32212	NJ 31780	NO 29893	NO 27717	NO 23830	NO 28053	NO 29660	NN 08328	NN 05740	NN 08407	NN 03710	NN 02225	NN 08559	NN 09480	NN 10307	NN 07761	NN 08172
reference	83983	83993	87958	83994	87174	85606	85133	83956	87121	29977	35478	30073	33167	33768	39219	36685	44834	28095	28066
Trace elements analysed via ICP-MS																			

\* trace elements analysed by ICP-MS

Appendix 2b

Zircon oxygen isotope data of the Lochnagar pluton and average values of bracketing zircon standard 91500

analyses no.	grain no.	$^{18}\text{O}/^{16}\text{O}$ (measured)	1 s.e.m.	$^{18}\text{O}/^{16}\text{O}$ (drift corrected)	$\delta^{18}\text{O}$ [‰] VSMOW	2SD	1 s.e.m.	n	grain area	comment
<u>Session 2 (31.05.2005)</u>										
AD2	91500 - 1 - 10		0.0020634	0.0000002	9.88	0.5	0.079	10		
	SA04/02 - 1	1	0.0020542	0.0000003	5.4		0.078	c2a	rejected, crack	
	SA04/02 - 2	2	0.0020577	0.0000004	7.1		0.133	c1a	rejected, crack	
	SA04/02 - 3	3	0.0020566	0.0000003	6.6		0.102	c2b		
	SA04/02 - 4	3	0.0020553	0.0000003	5.9		0.080	rim		
	SA04/02 - 5	3	0.0020567	0.0000002	6.6		0.069	c2a		
	SA04/02 - 6	5	0.0020557	0.0000004	6.1		0.106	c2a	rejected, crack	
	SA04/02 - 7	5	0.0020569	0.0000003	6.7		0.083	c2b		
	SA04/02 - 8	6	0.0020552	0.0000004	5.9		0.102	c2a		
	SA04/02 - 9	6	0.0020556	0.0000003	6.1		0.086	c2b		
	SA04/02 - 10	7	0.0020559	0.0000004	6.2		0.115	c1		
	91500 - 11 - 14		0.0020634	0.0000005	9.84	0.5	0.128	4		
	SA04/02 - 11	7	0.0020559	0.0000005	6.2			c2b	rejected, partly overlaps epoxy	
	SA04/02 - 12	7	0.0020552	0.0000002	5.9		0.065	c2a	rejected, crack	
	SA04/02 - 13	8	0.0020552	0.0000004	5.9		0.114	c2c		
	SA04/02 - 14	8	0.0020568	0.0000003	6.7		0.101	c2a	rejected, crack	
	SA04/02 - 15	8	0.0020556	0.0000004	6.1		0.106	c2b	rejected, crack	
	SA04/02 - 16	9	0.0020559	0.0000004	6.2		0.115	c1b		
	SA04/02 - 17	9	0.0020559	0.0000003	6.2		0.082	c1a		
	SA04/02 - 18	9	0.0020578	0.0000005	7.2		0.157	c2		
	SA04/02 - 19	10	0.0020574	0.0000003	6.9		0.116	c2		
	SA04/02 - 20	10	0.0020565	0.0000002	6.5		0.073	c1		
	91500 - 22 - 25		0.0020634	0.0000004	9.84	0.8	0.207	4		
	SA04/02 - 21	11	0.0020574	0.0000003	8.0		0.133	rim	rejected, crack	
	SA04/02 - 22	11	0.0020538	0.0000005	6.3		0.138	c1b		
	SA04/02 - 23	11	0.0020562	0.0000003	7.5		0.121	c1a		
	SA04/02 - 24	11	0.0020557	0.0000003	7.2		0.101	c1c		
	SA04/02 - 25	11	0.0020546	0.0000003	6.7		0.108	c1d		
	SA04/02 - 26	12	0.0020546	0.0000003	6.7		0.108	c1		
	SA04/02 - 27	13	0.0020525	0.0000003	5.7		0.086	rim	rejected, crack	
	SA04/02 - 28	13	0.0020542	0.0000003	6.5		0.107	c2b		
	SA04/02 - 29	13	0.0020555	0.0000004	7.1		0.134	c2a		
	SA04/02 - 30	14	0.0020535	0.0000004	6.2		0.113	c1		
<u>Session 3 (31.05.2005)</u>										
	91500 - 27 - 30		0.0020611	0.0000004	9.87	0.8	0.191	4		
	SA04/02 - 31	15	0.0020546	0.0000003	6.7		0.085	c2a		
	SA04/02 - 32	15	0.0020559	0.0000003	7.3		0.114	c2b		
	SA04/02 - 33	15	0.0020539	0.0000004	6.4		0.121	rim	rejected, crack	
	SA04/02 - 34	16	0.0020541	0.0000003	6.4		0.097	c2b		
	SA04/02 - 35	16	0.0020529	0.0000003	5.9		0.084	c2a		
	SA04/02 - 36	16	0.0020552	0.0000004	7.0		0.124	rim		
	SA04/02 - 37	17	0.0020551	0.0000004	6.9		0.120	c1b		
	SA04/02 - 38	17	0.0020544	0.0000004	6.6		0.128	c1a		
	SA04/02 - 39	18	0.0020561	0.0000004	7.4		0.157	rim		
	SA04/02 - 40	18	0.0020533	0.0000002	6.1		0.060	c1		
	91500 - 31 - 35		0.0020611	0.0000001	9.85	0.3	0.069	5		
	<u>Session 4 (01.06.2005)</u>									
	91500/18 - 11 - 20		0.0020157	0.0000002	9.78	0.5	0.079	10		
	91500/18 - 21, 23 - 30		0.0020159	0.0000001	9.89	0.4	0.071	9		
	91500 - 36 - 45		0.0020160	0.0000001	9.92	0.3	0.054	10		
	SA04/02 - 41	19	0.0020087	0.0000002	6.3		0.075	c1		
	SA04/02 - 42	19	0.0020085	0.0000003	6.2		0.093	rim	rejected, crack	
	SA04/02 - 43	1	0.0020089	0.0000003	6.4		0.109	c1b		
	SA04/02 - 44	2	0.0020076	0.0000003	5.8		0.087	c2b	rejected, crack	
	SA04/01 - 1	1	0.0020100	0.0000004	6.9		0.138	c2a		
AD1	SA04/01 - 2	1	0.0020109	0.0000003	7.4		0.126	c2b	rejected, crack	
	SA04/01 - 3	2	0.0020085	0.0000002	6.2		0.069	rim	rejected, crack	
	SA04/01 - 4	2	0.0020089	0.0000003	6.4		0.092	c2a	rejected, crack	
	SA04/01 - 5	3	0.0020103	0.0000003	7.1		0.117	c2		
	SA04/01 - 6	3	0.0020094	0.0000004	6.6		0.126	c1		
	<u>Session 5 (01.06.2005)</u>									
	91500 - 46 - 50		0.0020148	0.0000001	9.92	0.2	0.049	5		
	SA04/01 - 7	4	0.0020095	0.0000002	7.3		0.070	?		
	SA04/01 - 8	4	0.0020097	0.0000002	7.4		0.080	?		
	SA04/01 - 9	4	0.0020095	0.0000004	7.3		0.145	?		
	SA04/01 - 10	4	0.0020103	0.0000003	7.7		0.129	?		
	SA04/01 - 11	5	0.0020100	0.0000003	7.5		0.098	r1		

Appendix 2b

Zircon oxygen isotope data of the Lochnagar pluton and average values of bracketing zircon standard 91500

analyses no.	grain no.	$^{18}\text{O}/^{16}\text{O}$ (measured)	1 s.e.m.	$^{18}\text{O}/^{16}\text{O}$ (drift corrected)	$\delta^{18}\text{O}$ [‰] VSMOW	2SD	1 s.e.m.	n	grain area	comment
SA04/01 - 12	5	0.0020098	0.0000003		7.4		0.124		c1a	
SA04/01 - 13	5	0.0020092	0.0000002		7.1		0.083		c1b	rejected, crack
SA04/01 - 14	6	0.0020096	0.0000003		7.3		0.114		c2a	
SA04/01 - 15	6	0.0020094	0.0000003		7.3		0.126		c2b	
SA04/01 - 16	7	0.0020092	0.0000003		7.2		0.124		c1a	
91500 - 51-55		0.0020145	0.0000002		9.76	0.5	0.107	5		
91500 - 67-70		0.0020148	0.0000003		9.91	0.6	0.152	4		
SA04/01 - 17	7	0.0020100	0.0000003		7.5		0.106		c1b	
SA04/01 - 18	7	0.0020101	0.0000002		7.6		0.078		r1a	
SA04/01 - 19	7	0.0020099	0.0000004		7.5		0.148		r1b	
SA04/01 - 20	8	0.0020085	0.0000004		6.8		0.130		c1	
SA04/01 - 22	8	0.0020086	0.0000001		6.9		0.049		c2a	
SA04/01 - 23	8	0.0020095	0.0000002		7.3		0.084		c2b	
SA04/01 - 24	8	0.0020092	0.0000003		7.1		0.097		c2c	
SA04/01 - 25	8	0.0020100	0.0000003		7.5		0.126		r1a	
SA04/01 - 26	8	0.0020069	0.0000002		6.0		0.048		r1b	rejected, overlaps epoxy
SA04/01 - 27	9	0.0020080	0.0000002		6.5		0.051		c1	rejected, correction on position of secondary ion beam anomalously large
91500 - 71-75		0.0020147	0.0000002		9.86	0.4	0.084	5		
SA04/01 - 28	9	0.0020078	0.0000002		6.5		0.058		c2a	
SA04/01 - 29	9	0.0020094	0.0000003		7.3		0.116		c2b	
SA04/01 - 30	10	0.0020095	0.0000003		7.3		0.093		r1	rejected, correction on position of secondary ion beam anomalously large
SA04/01 - 31	10	0.0020081	0.0000002		6.6		0.059		c2	
SA04/01 - 32	10	0.0020106	0.0000004		7.8		0.150		c1	
SA04/01 - 33	11	0.0020112	0.0000002		8.1		0.082		r1	
SA04/01 - 34	11	0.0020094	0.0000003		7.2		0.118		c1	
SA04/01 - 35	12	0.0020098	0.0000003		7.5		0.098		c2a	
SA04/01 - 36	12	0.0020096	0.0000003		7.3		0.092		c1b	
SA04/01 - 37	12	0.0020108	0.0000003		8.0		0.108		c1c	rejected, convoluted, possibly altered area
<b>Session 6 (01.06.2005)</b>										
91500 - 76-80		0.0020156	0.0000001		9.90	0.3	0.070	5		
SA04/01 - 38	12	0.0020101	0.0000003		7.2		0.104		c1d	rejected, crack
SA04/01 - 39	12	0.0020105	0.0000003		7.4		0.120		c1a	
SA04/01 - 40	12	0.0020110	0.0000004		7.6		0.135		c2b	rejected, crack
SA04/01 - 41	13	0.0020080	0.0000002		6.2		0.060		c2a	
SA04/01 - 42	13	0.0020090	0.0000003		6.6		0.093		c2b	
SA04/01 - 43	14	0.0020094	0.0000002		6.8		0.083		c1	
SA04/01 - 44	14	0.0020090	0.0000003		6.6		0.106		c2a	
SA04/01 - 45	14	0.0020097	0.0000002		7.0		0.052		c2b	
SA04/01 - 46	15	0.0020092	0.0000003		6.7		0.102		c1	
SA04/01 - 47	15	0.0020097	0.0000001		7.0		0.046		c3	
91500 - 81, 83-85		0.0020154	0.0000002		9.81	0.3	0.081	4		
SA04/01 - 48	15	0.0020094	0.0000002		6.8		0.064		c2b	
SA04/01 - 49	15	0.0020090	0.0000002		6.6		0.069		c2a	
SA04/01 - 50	16	0.0020080	0.0000002		6.1		0.066		r1	
SA04/01 - 51	16	0.0020085	0.0000003		6.4		0.090		c1	
SA04/01 - 52	16	0.0020087	0.0000002		6.5		0.074		r3	
<b>L1-03</b> S04/03 - 1	1	0.0020070	0.0000003		5.6		0.094		r2	rejected, analytical problems
S04/03 - 2	1	0.0020089	0.0000003		6.6		0.111		c2	rejected, analytical problems
S04/03 - 3	1	0.0020071	0.0000004		5.7		0.124		r1	rejected, analytical problems
S04/03 - 4	2	0.0020055	0.0000003		4.9		0.083		c2	rejected, analytical problems
S04/03 - 5	2	0.0020055	0.0000003		4.9		0.066		r2	rejected, analytical problems
<b>Session 7 (01.06.2005)</b>										
91500 - 96-100		0.0020147	0.0000002		10.00	0.5	0.105	5		
S04/03 - 6	3	0.0020090	0.0000003		7.1		0.101		c2	
S04/03 - 7	4	0.0020085	0.0000004		6.9		0.133		c1	
S04/03 - 8	4	0.0020085	0.0000002		6.9		0.073		r1	
S04/03 - 9	6	0.0020077	0.0000002		6.5		0.081		c2a	
S04/03 - 11	6	0.0020082	0.0000003		6.7		0.092		c2b	
S04/03 - 12	7	0.0020084	0.0000003		6.8		0.093		c2	
S04/03 - 13	8	0.0020082	0.0000003		6.8		0.107		c1	
S04/03 - 14	8	0.0020083	0.0000001		6.8		0.048		r1	
S04/03 - 15	9	0.0020079	0.0000003		6.6		0.107		c2a	
S04/03 - 16	9	0.0020083	0.0000003		6.8		0.092		c2b	

Appendix 2b

Zircon oxygen isotope data of the Lochnagar pluton and average values of bracketing zircon standard 91500

analyses no.	grain no.	$^{18}\text{O}/^{16}\text{O}$ (measured)	1 s.e.m.	$^{18}\text{O}/^{16}\text{O}$ (drift corrected)	$\delta^{18}\text{O}$ [‰] VSMOW	2SD	1 s.e.m.	n	grain area	comment
91500 - 101-105		0.0020144	0.0000001		9.81	0.2	0.039	5		
91500/18 - 31-39		0.0020144	0.0000002		9.82	0.5	0.078	10		
<u>Session 8 (02.06.2005)</u>										
91500 - 106-115		0.0020136	0.0000003		9.95	0.8	0.125	10		
91500 - 120-129		0.0020132	0.0000008		9.77	0.8	0.119	10		
S04/03 - 17	10	0.0020077	0.0000003		7.0		0.113		c1	
S04/03 - 18	11	0.0020049	0.0000003		5.6		0.086		c2	
S04/03 - 19	12	0.0020042	0.0000004		5.3		0.097		rim	
S04/03 - 20	12	0.0020043	0.0000003		5.3		0.084		c1	rejected, crack
S04/03 - 21	13	0.0020052	0.0000003		5.8		0.081		c1	rejected, crack
S04/03 - 22	13	0.0020054	0.0000003		5.9		0.099		rim	
S04/03 - 23	14	0.0020063	0.0000001		6.3		0.042		c2a	
S04/03 - 24	14	0.0020051	0.0000003		5.7		0.086		c2b	
S04/03 - 25	14	0.0020055	0.0000003		5.9		0.086		rim	
S04/03 - 26	15	0.0020048	0.0000004		5.6		0.110		c1	
<u>Session 9 (02.06.2005)</u>										
91500 - 140-149		0.0020149	0.0000002		9.96	0.5	0.082	10		
S04/03 - 27	15	0.0020073	0.0000002		6.2		0.056		rim	
S04/03 - 28	16	0.0020078	0.0000003		6.4		0.100		c2	rejected, crack
S04/03 - 29	16	0.0020087	0.0000002		6.9		0.060		rim	
S04/03 - 32	18	0.0020093	0.0000002		7.2		0.082		rim	rejected, crack
S04/03 - 33	18	0.0020120	0.0000003		8.5		0.127		c2	rejected, crack
S04/03 - 36	20	0.0020063	0.0000003		5.7		0.075		c2a	rejected, correction on position of secondary ion beam anomalously large
S04/03 - 37	20	0.0020066	0.0000003		5.8		0.086		c2b	
S04/03 - 38	20	0.0020080	0.0000003		6.5		0.092		r2	
S04/03 - 39	21	0.0020081	0.0000002		6.6		0.070		r3	
S04/03 - 40	21	0.0020084	0.0000002		6.7		0.058		r1a	
91500 - 150-154		0.0020148	0.0000002		9.88	0.4	0.087	5		
S04/03 - 41	21	0.0020073	0.0000002		6.2		0.053		r1b	
S04/03 - 42	22	0.0020071	0.0000002		6.1		0.062		c1	
S04/03 - 43	23	0.0020072	0.0000002		6.1		0.068		c2a	
S04/03 - 44	23	0.0020082	0.0000002		6.6		0.076		c2b	
S04/03 - 45	24	0.0020081	0.0000001		6.6		0.044		c2	rejected, crack
S04/03 - 46	24	0.0020080	0.0000003		6.5		0.103		rim	
S04/03 - 48	25	0.0020066	0.0000004		5.8		0.112		r2	rejected, crack
S04/03 - 49	25	0.0020077	0.0000002		6.4		0.072		c2	
S04/03 - 50	25	0.0020078	0.0000003		6.4		0.094		r3	
S04/03 - 51	26	0.0020092	0.0000003		7.1		0.094		c1	
91500 - 155-159		0.0020145	0.0000002		9.77	0.4	0.084	5		
S04/03 - 52	26	0.0020080	0.0000003		6.5		0.089		c2	
S04/03 - 53	26	0.0020085	0.0000003		6.8		0.085		rim	
S04/03 - 54	27	0.0020080	0.0000002		6.6		0.065		c2	
S04/03 - 55	27	0.0020077	0.0000001		6.4		0.035		c1	
CnG	SA04/13 - 1	1	0.0020093	0.0000002	7.2		0.082		c2a	rejected, analytical problem
	SA04/13 - 2	1	0.0020048	0.0000002	4.9		0.058		c2b	rejected, analytical problem
	SA04/13 - 3	2	0.0020077	0.0000002	6.4		0.072		c2b	
	SA04/13 - 4	2	0.0020067	0.0000003	5.9		0.082		c2a	
	SA04/13 - 5	2	0.0020071	0.0000003	6.1		0.085		c1	
	SA04/13 - 6	3	0.0020067	0.0000003	5.9		0.095		c2	
	91500 - 161-164		0.0020148	0.0000003	9.89	0.6	0.161	4		
	SA04/13 - 7	4	0.0020061	0.0000004	5.6		0.099		r1	
	SA04/13 - 8	4	0.0020076	0.0000002	6.3		0.061		c1a	
	SA04/13 - 9	5	0.0020066	0.0000003	5.9		0.077		c2	
	SA04/13 - 10	5	0.0020074	0.0000003	6.2		0.080		c1	
	SA04/13 - 11	5	0.0020068	0.0000003	5.9		0.077		r1	
	SA04/13 - 12	6	0.0020066	0.0000003	5.8		0.076		c1a	
	SA04/13 - 13	6	0.0020051	0.0000005	5.1		0.123		c1b	rejected, crack
	SA04/13 - 14	6	0.0020071	0.0000004	6.1		0.117		r1	
	SA04/13 - 15	7	0.0020075	0.0000001	6.3		0.038		c1a	
	SA04/13 - 16	7	0.0020069	0.0000003	6.0		0.095		r2	
	SA04/13 - 17	7	0.0020068	0.0000001	5.9		0.041		c1b	
	SA04/13 - 18	8	0.0020068	0.0000003	5.9		0.084		r2	
	SA04/13 - 19	8	0.0020067	0.0000003	5.9		0.093		r1c	
	SA04/13 - 20	8	0.0020064	0.0000003	5.8		0.089		r1b	
	SA04/13 - 21	8	0.0020083	0.0000001	6.7		0.048		r1a	rejected, crack
	SA04/13 - 22	8	0.0020065	0.0000001	5.8		0.037		c1	
	SA04/13 - 24	9	0.0020066	0.0000002	5.8		0.049		c1	
	SA04/13 - 25	9	0.0020071	0.0000004	6.1		0.109		r1	

Appendix 2b

Zircon oxygen isotope data of the Lochnagar pluton and average values of bracketing zircon standard 91500

analyses no.	grain no.	$^{18}\text{O}/^{16}\text{O}$ (measured)	1 s.e.m.	$^{18}\text{O}/^{16}\text{O}$ (drift corrected)	$\delta^{18}\text{O}$ [‰] VSMOW	2SD	1 s.e.m.	n	grain area	comment
SA04/13 - 26	10	0.0020059	0.0000001		5.5	0.038			c2	rejected, correction on position of secondary ion beam anomalously large
91500 - 170-174		0.0020147	0.0000002		9.87	0.4	0.089	5		
SA04/13 - 27	10	0.0020072	0.0000003		6.1	0.098			c1	rejected, correction on position of secondary ion beam anomalously large
SA04/13 - 28	11	0.0020073	0.0000003		6.2	0.077			c1	
SA04/13 - 29	12	0.0020066	0.0000003		5.8	0.077			r1	
SA04/13 - 30	12	0.0020059	0.0000003		5.5	0.069			c1	
SA04/13 - 31	13	0.0020064	0.0000002		5.7	0.065			c1	
SA04/13 - 32	13	0.0020063	0.0000003		5.7	0.090			c2	
SA04/13 - 33	13	0.0020064	0.0000003		5.8	0.078			r1	
SA04/13 - 34	14	0.0020060	0.0000002		5.5	0.066			c2	
SA04/13 - 35	15	0.0020061	0.0000002		5.6	0.061			c1	
SA04/13 - 36	15	0.0020073	0.0000002		6.2	0.074			r1	
91500 - 175-179		0.0020145	0.0000004		9.74	0.9	0.193	5		
SA04/13 - 37	16	0.0020066	0.0000002		5.8	0.057			c1	
SA04/13 - 38	17	0.0020077	0.0000003		6.4	0.092			c1a	
SA04/13 - 39	17	0.0020077	0.0000003		6.4	0.107			c1b	
SA04/13 - 40	17	0.0020076	0.0000002		6.3	0.064			c2	
SA04/13 - 41	18	0.0020069	0.0000003		6.0	0.080			c2a	rejected, crack
SA04/13 - 42	18	0.0020063	0.0000003		5.7	0.079			c2b	rejected, crack
SA04/13 - 43	18	0.0020073	0.0000003		6.2	0.104			r1	
SA04/13 - 44	19	0.0020076	0.0000003		6.3	0.087			c1	
SA04/13 - 45	19	0.0020067	0.0000002		5.9	0.051			r1	
SA04/13 - 46	3	0.0020080	0.0000002		6.5	0.074			c2c	rejected, crack
91500 - 181-184		0.0020146	0.0000003		9.80	0.7	0.166	4		
<u>Session 10 (03.06.2005)</u>										
91500/18 - 42-44, 46-49		0.0020134	0.0000002	0.0020131	10.01	0.4	0.078	7		
91500 - 11-20		0.0020130	0.0000001	0.0020131	9.79	0.3	0.041	10		
91500 - 16, 17, 19, 20		0.0020133	0.0000002	0.0020131	9.92	0.4	0.094	4		
<b>L2-04</b>	<b>SA04/04 - 1</b>	1	0.0020036	0.0000003	5.1	0.079			c2b	rejected, crack
	SA04/04 - 2	1	0.0020073	0.0000002	7.0	0.063			c2a	
	SA04/04 - 3	2	0.0020091	0.0000006	7.9	0.236			c2a	
	SA04/04 - 4	2	0.0020080	0.0000001	7.3	0.052			c2b	
	SA04/04 - 5	2	0.0020061	0.0000002	6.3	0.060			rim	rejected, crack
	SA04/04 - 6	3	0.0020082	0.0000003	7.4	0.097			c1	rejected, crack
	SA04/04 - 7	3	0.0020090	0.0000005	7.8	0.198			r1	rejected, crack
	91500 - 21-25		0.0020133	0.0000002	9.96	0.6	0.123	5		
	SA04/04 - 10	5	0.0020074	0.0000002	7.0	0.064			c2a	
	SA04/04 - 11	5	0.0020086	0.0000002	7.6	0.080			c2b	
	SA04/04 - 13	7	0.0020077	0.0000003	7.2	0.114			c1	rejected, crack
	SA04/04 - 14	7	0.0020070	0.0000003	6.8	0.103			r1	rejected, crack
	SA04/04 - 15	7	0.0020078	0.0000002	7.2	0.087			r2	rejected, crack
	SA04/04 - 18	9	0.0020077	0.0000004	7.1	0.137			c2	rejected, crack
	SA04/04 - 19	9	0.0020094	0.0000003	8.0	0.112			r1	rejected, crack
	SA04/04 - 20	10	0.0020091	0.0000003	7.9	0.132			c1	
	SA04/04 - 21	10	0.0020122	0.0000003	9.4	0.154			r1	rejected, crack
	SA04/04 - 22	11	0.0020083	0.0000004	7.4	0.141			c1	
	91500 - 31-35		0.0020135	0.0000003	10.03	0.6	0.132	5		
	SA04/04 - 24	13	0.0020081	0.0000003	7.4	0.108			c1	
	SA04/04 - 25	13	0.0020089	0.0000002	7.8	0.091			r1a	
	SA04/04 - 26	13	0.0020087	0.0000002	7.7	0.076			r1b	rejected, crack
	SA04/04 - 28	15	0.0020063	0.0000002	6.5	0.079			c1	inherited
	SA04/04 - 29	15	0.0020054	0.0000002	6.0	0.074			c2a	inherited
	SA04/04 - 30	15	0.0020058	0.0000002	6.2	0.060			c2b	inherited
	SA04/04 - 31	16	0.0020065	0.0000004	6.6	0.116			c1	
	SA04/04 - 32	16	0.0020080	0.0000002	7.3	0.057			rim	
	SA04/04 - 34	18	0.0020075	0.0000003	7.1	0.091			c1	
	SA04/04 - 35	18	0.0020077	0.0000002	7.2	0.077			rim	
	SA04/04 - 21/2	10	0.0020102	0.0000002	8.4	0.072			r1	rejected, crack
	SA04/04 - 37	20	0.0020065	0.0000004	6.6	0.123			c1	rejected, crack
	SA04/04 - 38	20	0.0020079	0.0000002	7.3	0.087			c2	rejected, crack
	SA04/04 - 40	20	0.0020073	0.0000002	7.0	0.063			rim	rejected, crack
	SA04/04 - 43	23	0.0020084	0.0000002	7.5	0.071			c2	
	91500 - 36-40		0.0020133	0.0000003	9.93	0.6	0.124	5		
	SA04/04 - 45	22	0.0020073	0.0000002	6.9	0.062			r1	
<b>L3</b>	<b>SA04/05 - 1</b>	1	0.0020065	0.0000004	6.5	0.128			c1	rejected, crack
	SA04/05 - 2	1	0.0020070	0.0000004	6.8	0.136			rim	rejected, crack
	SA04/05 - 9	5	0.0020060	0.0000003	6.3	0.081			c1	

Appendix 2b

Zircon oxygen isotope data of the Lochnagar pluton and average values of bracketing zircon standard 91500

analyses no.	grain no.	$^{18}\text{O}/^{16}\text{O}$ (measured)	1 s.e.m.	$^{18}\text{O}/^{16}\text{O}$ (drift corrected)	$\delta^{18}\text{O}$ [‰] VSMOW	2SD	1 s.e.m.	n	grain area	comment
SA04/05 - 10	5	0.0020064	0.0000004		6.5		0.131		r1+r2	rejected, crack
SA04/05 - 7	4	0.0020079	0.0000005		7.3		0.165		c1+c2	
SA04/05 - 8	4	0.0020090	0.0000002		7.8		0.090		c2	
SA04/05 - 14	8	0.0020077	0.0000002		7.2		0.084		c1	
SA04/05 - 15	8	0.0020073	0.0000003		6.9		0.108		c2	rejected, crack
SA04/05 - 16	9	0.0020068	0.0000004		6.7		0.122		c2a	
91500 - 47, 49-51		0.0020136	0.0000002	0.0020131	10.07	0.5	0.116	4		
SA04/05 - 17	9	0.0020066	0.0000003		6.6		0.092		c2b	
SA04/05 - 21	11	0.0020070	0.0000003		6.8		0.103		c2a	
SA04/05 - 22	11	0.0020055	0.0000002		6.1		0.058		c2b	
SA04/05 - 26	14	0.0020068	0.0000004		6.7		0.139		c1	
SA04/05 - 27	14	0.0020066	0.0000002		6.6		0.072		rim	
SA04/05 - 30	16	0.0020066	0.0000003		6.6		0.100		c1	rejected, crack
SA04/05 - 31	16	0.0020073	0.0000002		7.0		0.055		rim	
SA04/05 - 34	18	0.0020046	0.0000003		5.6		0.094		c2a	
SA04/05 - 35	18	0.0020096	0.0000003		8.1		0.114		c2b	
SA04/05 - 36	19	0.0020078	0.0000003		7.2		0.106		c2a	
SA04/05 - 37	19	0.0020074	0.0000002		7.0		0.059		c2b	
SA04/05 - 40	21	0.0020069	0.0000003		6.7		0.089		c2	
SA04/05 - 41	21	0.0020058	0.0000002		6.2		0.059		rim	
SA04/05 - 47	24	0.0020068	0.0000002		6.7		0.064		c2	rejected, crack
SA04/05 - 48	24	0.0020046	0.0000003		5.6		0.073		rim	
91500 - 52-56		0.0020132	0.0000002	0.0020131	9.91	0.4	0.098	5		
SA04/05 - 49	25	0.0020056	0.0000002		6.1		0.065		c2b	
SA04/05 - 50	25	0.0020079	0.0000002		7.3		0.074		c2a	
SA04/05 - 51	26	0.0020091	0.0000002		7.9		0.094		c1	rejected, correction on position of secondary ion beam anomalously large
SA04/05 - 52	26	0.0020062	0.0000003		6.4		0.084		rim	rejected, correction on position of secondary ion beam anomalously large
SA04/05 - 55	28	0.0020049	0.0000002		5.8		0.068		c2	rejected, crack
SA04/05 - 56	28	0.0020075	0.0000002		7.1		0.062		rim	rejected, crack
L1-06 SA04/06 - 1	1	0.0020063	0.0000004		6.5		0.127		c1	
SA04/06 - 2	2	0.0020064	0.0000003		6.5		0.099		c1	
SA04/06 - 3	3	0.0020068	0.0000002		6.7		0.058		c1	
SA04/06 - 6	5	0.0020070	0.0000002		6.8		0.077		c1	
SA04/06 - 7	5	0.0020050	0.0000002		5.8		0.064		c2	
SA04/06 - 10	7	0.0020064	0.0000004		6.5		0.131		c1	
SA04/06 - 11	7	0.0020064	0.0000002		6.5		0.050		c2	
SA04/06 - 17	12	0.0020080	0.0000002		7.3		0.079		c1	rejected, crack
SA04/06 - 18	13	0.0020064	0.0000003		6.5		0.086		c1	
91500 - 58-61		0.0020133	0.0000004	0.0020131	9.92	0.7	0.175	4		
SA04/06 - 23	18	0.0020053	0.0000002		5.9		0.050		c2	
SA04/06 - 44	36	0.0020047	0.0000004		5.7		0.113		c1	
SA04/06 - 45	36	0.0020063	0.0000001		6.5		0.048		rim	rejected, crack
SA04/06 - 41	34	0.0020054	0.0000002		6.0		0.052		r2	rejected, crack
SA04/06 - 42	34	0.0020059	0.0000003		6.3		0.096		r1b	rejected, crack
SA04/06 - 36	30	0.0020084	0.0000003		7.5		0.118		c1	rejected, crack
SA04/06 - 37	30	0.0020062	0.0000003		6.4		0.098		c2	
SA04/06 - 43	35	0.0020030	0.0000004		4.8		0.092		c2	
SA04/06 - 39	32	0.0020060	0.0000003		6.3		0.082		c1b	
SA04/06 - 46	32	0.0020068	0.0000003		6.7		0.086		c1a	rejected, crack
91500 - 62-66		0.0020135	0.0000002	0.0020131	10.03	0.5	0.104	5		
Session 15 (05.06.2005)										
91500 - 127-131		0.0020095	0.0000002		9.87	0.5	0.102	5		
L2-12 SA04/12 - 1	1	0.0020022			6.2				c1	rejected, correction on position of secondary ion beam anomalously large
			0.0000006				0.179			
SA04/12 - 2	1	0.0020020	0.0000004		6.1		0.120		c2	
SA04/12 - 3	2	0.0020020	0.0000005		6.2		0.142		c2	
SA04/12 - 4	3	0.0020020	0.0000002		6.1		0.075		c2a	
SA04/12 - 5	3	0.0020017	0.0000002		6.0		0.052		c2b	
SA04/12 - 6	4	0.0020021	0.0000002		6.2		0.065		c2c	
SA04/12 - 7	4	0.0020026	0.0000003		6.4		0.112		c2b	rejected, crack
SA04/12 - 8	4	0.0020033	0.0000004		6.8		0.126		c2a	rejected, crack
SA04/12 - 9	5	0.0020039	0.0000003		7.1		0.113		c1	
SA04/12 - 10	5	0.0020031	0.0000004		6.7		0.137		c2	
SA04/12 - 19	9	0.0020027	0.0000003		6.5		0.104		c2b	
SA04/12 - 20	9	0.0020039	0.0000003		7.1		0.104		c2a	
SA04/12 - 24	10	0.0020006	0.0000004		5.5		0.106		c2a	rejected, crack
91500 - 132-135		0.0020097	0.0000002		9.99	0.3	0.082	4		

Appendix 2b

Zircon oxygen isotope data of the Lochnagar pluton and average values of bracketing zircon standard 91500

analyses no.	grain no.	$^{18}\text{O}/^{16}\text{O}$ (measured)	1 s.e.m.	$^{18}\text{O}/^{16}\text{O}$ (drift corrected)	$\delta^{18}\text{O}$ [‰] VSMOW	2SD	1 s.e.m.	n	grain area	comment
SA04/12 - 22	10	0.0019989	0.0000004		4.6		0.103		c2b	rejected, correction on position of secondary ion beam anomalously large
SA04/12 - 23	10	0.0020007	0.0000005		5.5		0.142		c1	rejected, crack
SA04/12 - 25	11	0.0020042	0.0000004		7.3		0.130		c2a	
SA04/12 - 26	11	0.0020036	0.0000005		6.9		0.166		c2b	
SA04/12 - 27	11	0.0020031	0.0000003		6.7		0.087		c2c	
SA04/12 - 32	13	0.0020017	0.0000004		6.0		0.127		c2b	rejected, correction on position of secondary ion beam anomalously large
SA04/12 - 33	13	0.0020010	0.0000004		5.7		0.120		c2c	rejected, crack
SA04/12 - 34	14	0.0020002	0.0000004		5.2		0.110		c1b	rejected, crack
SA04/12 - 35	14	0.0019990	0.0000004		4.6		0.100		c1a	rejected, crack
SA04/12 - 37	15	0.0020005	0.0000005		5.4		0.141		c1	
SA04/12 - 38	15	0.0020007	0.0000004		5.5		0.107		c2	
91500 - 137, 139-141		0.0020092	0.0000001		9.71	0.3	0.064	4		
<u>Session 2 (24.04.2006)</u>										
91500/1 - 31-40		0.0020128	0.0000002		9.77	0.7	0.112	10		
91500/1 - 41-45, 47-50		0.0020121	0.0000003		9.47	0.9	0.142	9		
91500/2 - 1-10		0.0020133	0.0000002		10.04	0.6	0.094	10		
L2-15 SA04/15 - 1a	1	0.0020095			8.2				c1	rejected, correction on position of secondary ion beam anomalously large
			0.0000002				0.089			
SA04/15 - 2a	2	0.0020047	0.0000002		5.7		0.051		c2b	rejected, crack
SA04/15 - 3a	3	0.0020054	0.0000003		6.1		0.088		c2a	
SA04/15 - 4a	4	0.0020033	0.0000003		5.1		0.074		c2a	rejected, possibly altered
SA04/15 - 5b	5	0.0020062	0.0000004		6.5		0.137		r1b	rejected, crack
SA04/15 - 5a	5	0.0020067	0.0000003		6.8		0.115		r1a	
SA04/15 - 6a	6	0.0020051	0.0000003		6.0		0.104		c1	
SA04/15 - 7a	7	0.0020068	0.0000003		6.8		0.110		c2	rejected, correction on position of secondary ion beam anomalously large
91500/2 - 11-20		0.0020131	0.0000003		9.93	0.8	0.128	10		
SA04/15 - 7b	7	0.0020075	0.0000006		7.1		0.221		rim	
SA04/15 - 8a	8	0.0020049	0.0000002		5.9		0.046		c1	
SA04/15 - 9a	9	0.0020055	0.0000002		6.2		0.070		c2	
SA04/15 - 10a	10	0.0020063	0.0000004		6.6		0.131		c2	
SA04/15 - 12a	12	0.0020073	0.0000003		7.1		0.104		c2	
SA04/15 - 13a	13	0.0020071	0.0000002		7.0		0.061		c1	
SA04/15 - 13b	13	0.0020072	0.0000002		7.0		0.067		rim	
SA04/15 - 14a	14	0.0020072	0.0000003		7.0		0.109		c1	
SA04/15 - 14b	14	0.0020069	0.0000003		6.9		0.113		rim	rejected, crack
SA04/15 - 15a	15	0.0020061	0.0000004		6.5		0.114		c1b	rejected, crack
91500/2 - 21-30		0.0020134	0.0000003		10.11	0.8	0.131	10		
SA04/15 - 15b	15	0.0020058	0.0000003		6.3		0.109		rim	rejected, correction on position of secondary ion beam anomalously large
SA04/15 - 16a	16	0.0020014	0.0000003		4.1		0.053		c1a	
SA04/15 - 17a	17	0.0020072	0.0000003		7.0		0.102		c1	
SA04/15 - 17b	17	0.0020071	0.0000002		7.0		0.059		c2a	
SA04/15 - 17c	17	0.0020074	0.0000003		7.1		0.122		c2b	rejected, crack
SA04/15 - 18a	18	0.0020073	0.0000004		7.1		0.127		c2a	rejected, crack
SA04/15 - 18b	18	0.0020076	0.0000003		7.2		0.104		r1	rejected, crack
SA04/15 - 18c	18	0.0020108	0.0000004		8.8		0.156		r2a	rejected, crack
SA04/15 - 16b	16	0.0020019	0.0000002		4.4		0.037		c1b	
SA04/15 - 19a	19	0.0020060	0.0000002		6.4		0.059		c1	
91500/1 - 51-60		0.0020128	0.0000002		9.82	0.5	0.084	10		
SA04/15 - 20a	20	0.0020064	0.0000003		6.6		0.095		c1	rejected, correction on position of secondary ion beam anomalously large
SA04/15 - 21a	21	0.0020087	0.0000002		7.8		0.075		c1	
SA04/15 - 21b	21	0.0020070	0.0000001		6.9		0.040		c2	
SA04/15 - 22a	22	0.0020046	0.0000003		5.7		0.087		core a	inherited
SA04/15 - 26a	26	0.0020080	0.0000003		7.4		0.094		c1	rejected, crack
SA04/15 - 26c	26	0.0020075	0.0000004		7.2		0.128		r2	rejected, correction on position of secondary ion beam anomalously large
SA04/15 - 27a	27	0.0020033	0.0000004		5.1		0.094		c1a	rejected, possibly altered
SA04/15 - 27b	27	0.0020037	0.0000005		5.3		0.143		c1b	rejected, possibly altered

Appendix 2b

Zircon oxygen isotope data of the Lochnagar pluton and average values of bracketing zircon standard 91500

analyses no.	grain no.	$^{18}\text{O}/^{16}\text{O}$ (measured)	1 s.e.m.	$^{18}\text{O}/^{16}\text{O}$ (drift corrected)	$\delta^{18}\text{O}$ [‰] VSMOW	2SD	1 s.e.m.	n	grain area	comment
91500/1 - 61, 63-70		0.0020129	0.0000003		9.85	1.0	0.153	9		
Session 11 (19.06.2006)										
91500/12 - 11-20		0.0020166	0.0000001		9.86	0.4	0.064	10		
91500/12 - 31-40		0.0020166	0.0000001		9.83	0.4	0.071	10		
Mount1/91500 - 1-9		0.0020168	0.0000002		9.93	0.7	0.120	9		
Mount1/91500 - 20-21, 23-25		0.0020166	0.0000001		9.83	0.3	0.064	5		
Mount1/91500 - 26-30		0.0020166	0.0000004		9.83	0.9	0.206	5		
SA04/15 - 3b	3	0.0020092			6.2				c2b	rejected, possibly altered
SA04/15 - 28a	28	0.0020090			6.1				c1	
Session 13 (15.11.2006)										
91500 - 1-10		0.0020195	0.0000001	0.0020197	9.76	0.3	0.052	10		
91500 - 11-20		0.0020195	0.0000001	0.0020195	9.86	0.2	0.035	10		
SA04/15 - 33a	33	0.0020112	0.0000003		5.9		0.095		inh1	inherited
SA04/15 - 29a	29	0.0020106	0.0000005		5.5		0.134		inh1	inherited
SA04/15 - 29b	29	0.0020130	0.0000002		6.8		0.065		rim	rejected, crack
SA04/15 - 2a	2	0.0020131	0.0000003		6.8		0.100		c2b	rejected, crack
SA04/15 - 36a	36	0.0020098	0.0000003		5.2		0.073		c2	inherited
SA04/15 - 3b	3	0.0020129	0.0000003		6.7		0.096		c2b	rejected, crack
SA04/15 - 3a	3	0.0020119	0.0000004		6.2		0.114		c2a	
SA04/15 - 35a	35	0.0020133	0.0000002		6.9		0.074		c2b	rejected, possibly altered
SA04/15 - 35b	35	0.0020119	0.0000003		6.3		0.091		c2a	
SA04/15 - 5c	5	0.0020138	0.0000002		7.2		0.072		r1c	
91500 - 21-25, 27-30		0.0020195	0.0000001	0.0020190	10.11	0.4	0.060	9		
SA04/15 - 4a	4	0.0020113	0.0000002		6.1		0.055		c2a	
SA04/15 - 4b	4	0.0020119	0.0000005		6.4		0.148		c2b	
SA04/15 - 32a	32	0.0020104	0.0000007		5.7		0.208		c2a	inherited
SA04/15 - 32b	32	0.0020122	0.0000004		6.6		0.140		c2b	inherited
SA04/15 - 32c	32	0.0020091	0.0000012		5.0		0.304		c2c	inherited, rejected, crack
SA04/15 - 15c	15	0.0020122	0.0000003		6.6		0.104		c1a	
SA04/15 - 14b	14	0.0020139	0.0000023		7.4		0.832		rim	rejected, crack
SA04/15 - 16a	16	0.0020084	0.0000025		4.8		0.598		c1a	
SA04/15 - 17c	17	0.0020141	0.0000005		7.6		0.201		c2b	rejected, crack
SA04/15 - 18e	18	0.0020134	0.0000002		7.2		0.075		c2b	rejected, crack
SA04/15 - 18d	18	0.0020111	0.0000004		6.1		0.131		r2b	rejected, crack
SA04/15 - 22a	22	0.0020135	0.0000003		7.3		0.127		core a	inherited
SA04/15 - 22b	22	0.0020138	0.0000004		7.5		0.160		core b	inherited
91500 - 31-35		0.0020181	0.0000003	0.0020185	9.64	0.8	0.168	5		
91500 - 36-39		0.0020185	0.0000002	0.0020185	9.88	0.3	0.073	5		
91500 - 42-45		0.0020179	0.0000002	0.0020179	9.80	0.4	0.101	4		



## Appendix 2c

## Zircon U-Pb data of the Lochnagar pluton

sample	analysis no.	grain U no.	Th ppm	Th/U ppm	<sup>204</sup> Pb/ ppb (%)	<sup>204</sup> Pb/ ppb	corrected ratios				Ages (Ma)				comment			
							<sup>206</sup> Pb/ <sup>204</sup> Pb	1σ	<sup>206</sup> Pb/ <sup>204</sup> Pb	1σ	<sup>206</sup> Pb/ <sup>238</sup> U	1σ	<sup>206</sup> Pb/ <sup>238</sup> U	% disc				
AD1	SA04/01-3	2	376	126	25	0.34	0.04	0.000191	0.0551	0.0004	0.093	0.0013	0.5084	0.0053	0.0669	0.0005	0.72	
	SA04/01-4	2	116	46	8	0.41	18.0	4.99	0.0549	0.0035	0.1165	0.0019	0.4879	0.0319	0.0645	0.0010	0.23	rejected, high common Pb
	SA04/01-5	3	136	71	10	0.53	0.1	0.000064	0.0554	0.0007	0.1683	0.0011	0.5126	0.0079	0.0671	0.0006	0.54	c2
	SA04/01-6	3	97	61	7	0.64	1.6	0.53	0.0529	0.0013	0.1942	0.0032	0.4921	0.0126	0.0675	0.0006	0.36	rejected, > 10 % discordant
	SA04/01-15	6	141	139	11	0.61	0.3	0.06	0.0546	0.0007	0.3148	0.0023	0.5083	0.0077	0.0676	0.0006	0.57	c1
	SA04/01-14	6	105	75	8	0.73	0.8	0.25	0.0533	0.0008	0.2258	0.0033	0.5004	0.0089	0.0681	0.0006	0.48	rejected, > 10 % discordant
	SA04/01-20	8	136	121	10	0.91	0.3	0.06	0.0539	0.0008	0.2814	0.0021	0.4940	0.0084	0.0665	0.0005	0.47	c2
	SA04/01-23	8	79	60	6	0.78	0.0	0.0000002	0.0551	0.0009	0.2458	0.0022	0.5052	0.0098	0.0665	0.0006	0.47	c2
	SA04/01-26	8	173	129	13	0.77	0.2	0.03	0.0548	0.0006	0.2408	0.0013	0.5026	0.0065	0.0665	0.0005	0.57	rim
	SA04/01-27	9	72	60	6	0.85	0.2	0.07	0.0541	0.0011	0.2664	0.0028	0.4992	0.0110	0.0669	0.0007	0.46	c1
	SA04/01-28	9	94	92	7	1.00	0.4	0.14	0.0556	0.0009	0.3129	0.0028	0.5097	0.0094	0.0665	0.0006	0.48	c2a
	SA04/01-29	9	101	78	8	0.80	0.3	0.09	0.0546	0.0008	0.2520	0.0022	0.4988	0.0083	0.0664	0.0005	0.48	c2b
	SA04/01-33	11	268	278	22	1.06	0.4	0.05	0.0543	0.0007	0.3308	0.0028	0.5032	0.0073	0.0672	0.0005	0.50	r1
	SA04/01-34	11	157	214	14	1.40	0.6	0.12	0.0561	0.0006	0.4338	0.0046	0.5198	0.0065	0.0673	0.0005	0.61	c1
	SA04/01-43	14	89	65	7	0.75	0.0	0.0000667	0.0560	0.0008	0.2347	0.0022	0.5140	0.0087	0.0666	0.0007	0.58	c1
	SA04/01-44	14	76	41	5	0.56	0.2	0.07	0.0547	0.0011	0.1747	0.0022	0.5084	0.0116	0.0675	0.0008	0.40	c2
	SA04/01-46	15	124	226	12	1.87	0.0	0.01	0.0558	0.0006	0.5819	0.0040	0.5157	0.0070	0.0670	0.0008	0.61	c1
	SA04/01-48	15	151	130	12	0.88	0.5	0.11	0.0549	0.0010	0.2732	0.0020	0.5059	0.0097	0.0668	0.0005	0.42	c1
	SA04/01-51	16	446	1050	47	2.41	0.5	0.04	0.0556	0.0005	0.7549	0.0030	0.5176	0.0097	0.0675	0.0005	0.66	c2c
	SA04/01-52	16	216	448	22	2.12	0.9	0.13	0.0542	0.0005	0.6713	0.0060	0.5094	0.0081	0.0682	0.0005	0.61	rim
	SA04/01-7	4	234	252	19	1.11	0.7	0.10	0.0553	0.0007	0.3467	0.0022	0.5093	0.0081	0.0682	0.0006	0.52	?
	SA04/01-9	4	229	280	20	1.25	0.6	0.08	0.0548	0.0005	0.3904	0.0020	0.5278	0.0081	0.0689	0.0008	0.83	?
	SA04/01-10	4	100	87	8	0.89	0.2	0.05	0.0555	0.0010	0.2776	0.0020	0.5223	0.0075	0.0683	0.0006	0.44	c2a
	SA04/01-42	2	147	68	10	0.48	0.2	0.04	0.0555	0.0006	0.1504	0.0013	0.5069	0.0077	0.0663	0.0007	0.66	c2b
AD2	SA04/02-39	18	1061	994	82	0.96	9.9	0.30	0.0551	0.0004	0.3035	0.0022	0.5033	0.0052	0.0663	0.0005	0.71	rim
	SA04/02-40	18	2590	5221	262	2.07	0.8	0.01	0.0554	0.0001	0.6462	0.0011	0.5264	0.0038	0.0689	0.0005	0.96	rejected, > 1000 ppm U
	SA04/02-26	12	1960	1839	155	0.96	0.9	0.01	0.0549	0.0002	0.3035	0.0006	0.5123	0.0039	0.0676	0.0005	0.93	c1
	SA04/02-45	12	617	1760	28	2.93	0.9	0.13	0.0587	0.0002	0.7676	0.0011	0.2120	0.0194	0.0262	0.0024	1.00	rejected, crack
	SA04/02-45.2	12	3116	7351	327	2.42	71.6	0.71	0.0556	0.0003	0.7732	0.0020	0.5240	0.0062	0.0684	0.0007	0.86	c1+rim
	SA04/02-19	10	550	466	42	0.87	1.2	0.07	0.0552	0.0003	0.7262	0.0011	0.5035	0.0058	0.0682	0.0007	0.89	c2
	SA04/02-20	10	2000	3675	192	1.89	0.0	0.00	0.0553	0.0002	0.5961	0.0010	0.5197	0.0056	0.0682	0.0007	0.95	c1
	SA04/02-41	19	962	1273	81	1.36	1.0	0.03	0.0556	0.0003	0.4301	0.0069	0.5089	0.0059	0.0684	0.0007	0.91	c1
	SA04/02-42	19	273	67	18	0.25	149.8	15.57	0.0449	0.0037	0.0629	0.0114	0.4030	0.0352	0.0651	0.0017	0.29	rim
	SA04/02-30	14	1299	1501	104	1.19	0.9	0.02	0.0556	0.0006	0.3797	0.0029	0.5044	0.0072	0.0657	0.0008	0.93	c1
	SA04/02-12	7	270	212	20	0.81	0.5	0.06	0.0542	0.0003	0.2525	0.0024	0.4835	0.0074	0.0647	0.0007	0.70	rejected, crack
	SA04/02-12	7	279	194	20	0.71	0.3	0.03	0.0553	0.0002	0.2260	0.0015	0.5064	0.0074	0.0663	0.0007	0.70	c2
	SA04/02-27	13	1891	2685	164	1.46	15.6	0.26	0.0552	0.0002	0.4645	0.0014	0.5110	0.0055	0.0671	0.0007	0.93	rejected, > 1000 ppm U
	SA04/02-29	13	306	49	20	0.16	0.4	0.05	0.0556	0.0005	0.0509	0.0011	0.5167	0.0074	0.0675	0.0007	0.73	c2
	SA04/02-31	15	446	344	34	0.79	0.7	0.05	0.0548	0.0004	0.2484	0.0033	0.5093	0.0068	0.0673	0.0007	0.79	c2a
	SA04/02-32	15	232	153	17	0.68	0.8	0.12	0.0545	0.0008	0.2138	0.0033	0.5014	0.0091	0.0667	0.0008	0.63	c2b
	SA04/02-46	20	1237	1730	111	1.43	0.2	0.01	0.0551	0.0003	0.4517	0.0070	0.5279	0.0060	0.0685	0.0007	0.90	c1
	SA04/02-22	11	354	245	26	0.71	2.1	0.19	0.0553	0.0002	0.4651	0.0009	0.5263	0.0068	0.0680	0.0007	0.92	c1b
	SA04/02-24	11	437	8	0.40	0.4	0.12	0.0001025	0.0542	0.0004	0.2239	0.0016	0.4938	0.0064	0.0681	0.0007	0.80	c1c
	SA04/02-25	11	119	47	8	0.18	0.7	0.07	0.0553	0.0009	0.1273	0.0019	0.4931	0.0097	0.0646	0.0008	0.60	c1d
	SA04/02-27.2	13	303	58	21	0.18	0.7	0.07	0.0551	0.0006	0.1656	0.0010	0.4988	0.0074	0.0656	0.0007	0.71	c2b
	SA04/02-47	21	335	160	21	0.94	1.5	0.16	0.0554	0.0006	0.1657	0.0040	0.4980	0.0074	0.0652	0.0007	0.73	c2a
	SA04/02-48	21	280	208	21	0.76	44.2	4.89	0.0542	0.0012	0.2352	0.0128	0.4971	0.0128	0.0665	0.0007	0.45	c2b
L1-03	SA04/03-13	8	934	837	73	0.92	0.9	0.03	0.0554	0.0003	0.2919	0.0023	0.5169	0.0044	0.0677	0.0005	0.82	c1+r1
	SA04/03-14	8	74	38	5	0.52	0.5	0.23	0.0553	0.0013	0.1592	0.0037	0.4999	0.0123	0.0655	0.0006	0.39	r1
	SA04/03-23	14	499	557	41	1.15	0.8	0.05	0.0547	0.0004	0.3623	0.0031	0.5049	0.0052	0.0670	0.0005	0.72	c2a

[illegible]





sample	analysis no.	grain no.	U ppm	Th ppm	<sup>204</sup> Pb/ <sup>206</sup> Pb ppb (%)	<sup>204</sup> Pb/ <sup>206</sup> Pb	corrected ratios				Ages (Ma)				grain comment			
							<sup>206</sup> Pb/ <sup>238</sup> Pb	1σ	<sup>206</sup> Pb/ <sup>238</sup> Pb	1σ	<sup>206</sup> Pb/ <sup>238</sup> Pb	1σ	<sup>206</sup> Pb/ <sup>238</sup> Pb	1σ				
91500		79	28	15	0.36	0.0	0.00000001	0.0753	0.0006	0.1080	0.0010	1.8541	0.0224	1.8541	0.0224	1.8541	0.016 76	
91500		82	29	15	0.36	0.0	0.00000001	0.0737	0.0006	0.1083	0.0007	1.8057	0.0231	1.777	0.018 07	1.7	-2	
91500		81	29	15	0.36	0.0	0.00000035	0.0756	0.0007	0.1078	0.0008	1.8760	0.0246	1.799	0.017 07	1.73	2	
91500		83	29	15	0.36	0.0	0.00000001	0.0743	0.0007	0.1083	0.0007	1.8553	0.0266	1.812	0.020 20	0.79	-2	
91500		82	29	15	0.36	0.0	0.00000001	0.0750	0.0006	0.1089	0.0008	1.8793	0.0241	1.800	0.018 07	1.77	2	
91500		80	28	15	0.36	0.0	0.00000034	0.0750	0.0007	0.1089	0.0008	1.8400	0.0259	1.778	0.019 19	0.76	1	
91500		83	30	15	0.36	0.3	0.04	0.0000207	0.0753	0.0008	0.1108	0.0009	1.8542	0.0268	1.785	0.018 07	1.72	2
91500		83	30	15	0.37	0.0	0.00000001	0.0753	0.0006	0.1112	0.0005	1.8468	0.0236	1.780	0.016 08	1.61	2	
91500		79	28	15	0.37	0.0	0.00000001	0.0746	0.0007	0.1105	0.0010	1.8380	0.0232	1.788	0.020 23	0.80	2	
91500		79	28	14	0.37	0.3	0.04	0.0000220	0.0752	0.0006	0.1111	0.0010	1.8462	0.0232	1.780	0.018 08	1.61	2
91500		82	29	15	0.36	0.0	0.00000001	0.0748	0.0007	0.1101	0.0007	1.8298	0.0249	1.774	0.017 07	1.72	2	
91500		83	29	15	0.37	0.0	0.00000001	0.0750	0.0006	0.1118	0.0005	1.8704	0.0241	1.810	0.019 08	1.60	2	
91500		80	29	15	0.37	0.5	0.08	0.0000415	0.0742	0.0007	0.1099	0.0013	1.8231	0.0257	1.783	0.018 07	1.71	-1
91500		80	29	15	0.37	0.8	0.12	0.0000666	0.0744	0.0007	0.1080	0.0017	1.8815	0.0257	1.833	0.020 08	0.77	-3
91500		81	30	15	0.37	0.0	0.00000001	0.0751	0.0007	0.1125	0.0007	1.8550	0.0336	1.792	0.020 28	0.87	2	
91500		85	29	16	0.35	0.4	0.06	0.0000311	0.0748	0.0007	0.1059	0.0010	1.9117	0.0331	1.853	0.020 26	0.82	2
91500		80	28	15	0.35	0.0	0.00000001	0.0749	0.0007	0.1066	0.0008	1.8308	0.0257	1.772	0.019 19	0.75	2	
91500		79	27	14	0.35	0.0	0.00000001	0.0741	0.0004	0.1066	0.0010	1.7951	0.0228	1.757	0.020 20	0.88	2	
91500		82	28	15	0.35	0.2	0.03	0.0000136	0.0743	0.0007	0.1071	0.0007	1.8366	0.0276	1.793	0.020 20	0.75	-1
91500		80	27	14	0.35	0.0	0.00000001	0.0736	0.0007	0.1075	0.0009	1.8308	0.0273	1.805	0.020 20	0.74	-4	
91500		80	28	15	0.36	0.4	0.06	0.0000343	0.0751	0.0007	0.1045	0.0012	1.8290	0.0253	1.766	0.018 07	1.75	2
91500		77	26	14	0.35	0.0	0.00000001	0.0754	0.0006	0.1074	0.0009	1.8745	0.0257	1.803	0.020 20	0.80	2	
91500		78	27	14	0.36	0.0	0.00000001	0.0744	0.0006	0.1073	0.0006	1.8279	0.0257	1.782	0.020 20	0.79	2	
91500		83	30	15	0.36	0.0	0.00000001	0.0747	0.0008	0.1095	0.0007	1.8372	0.0269	1.785	0.018 06	1.69	2	
91500		83	31	16	0.37	0.0	0.00000001	0.0749	0.0006	0.1117	0.0009	1.8623	0.0259	1.803	0.020 20	0.79	2	
91500		83	29	15	0.36	0.1	0.01	0.0000042	0.0755	0.0008	0.1086	0.0010	1.8701	0.0269	1.797	0.018 06	1.63	2
91500		84	29	15	0.36	0.0	0.00000001	0.0748	0.0006	0.1091	0.0006	1.8497	0.0231	1.793	0.016 07	1.74	0	
91500		78	27	14	0.36	0.0	0.00000001	0.0742	0.0007	0.1057	0.0009	1.8529	0.0244	1.797	0.016 06	1.68	2	
91500		80	28	15	0.35	0.0	0.00000001	0.0746	0.0006	0.1076	0.0007	1.8565	0.0232	1.814	0.017 07	1.74	-3	
91500		79	27	15	0.35	0.0	0.00000001	0.0756	0.0007	0.1076	0.0008	1.8763	0.0266	1.800	0.018 07	1.72	2	
91500		84	29	15	0.36	0.0	0.00000001	0.0736	0.0005	0.1078	0.0009	1.8003	0.0213	1.775	0.017 07	1.63	-2	
91500		80	27	15	0.35	0.3	0.05	0.0000258	0.0738	0.0006	0.1060	0.0012	1.8156	0.0236	1.784	0.017 07	1.75	-2
91500		78	27	14	0.35	0.0	0.00000001	0.0747	0.0008	0.1052	0.0007	1.8618	0.0281	1.809	0.019 06	1.69	2	
91500		80	27	15	0.35	0.0	0.00000001	0.0741	0.0006	0.1047	0.0010	1.8295	0.0218	1.791	0.017 07	1.78	-2	
91500		86	30	16	0.35	0.1	0.01	0.0000040	0.0749	0.0006	0.1077	0.0008	1.8145	0.0209	1.757	0.017 07	1.84	2
91500		81	28	15	0.35	0.0	0.00000001	0.0751	0.0006	0.1066	0.0008	1.8461	0.0215	1.782	0.016 04	1.69	2	
91500		81	28	15	0.35	0.0	0.00000001	0.0748	0.0008	0.1086	0.0010	1.8431	0.0255	1.787	0.016 06	1.64	2	
91500		82	28	15	0.36	0.1	0.01	0.0000052	0.0741	0.0009	0.1062	0.0009	1.8357	0.0278	1.796	0.015 04	1.54	2
91500		81	28	15	0.35	0.0	0.00000001	0.0744	0.0008	0.1058	0.0006	1.8446	0.0236	1.799	0.013 03	1.58	2	
91500		80	28	15	0.36	0.0	0.00000001	0.0763	0.0007	0.1062	0.0007	1.8828	0.0243	1.791	0.015 06	1.67	2	
91500		81	28	15	0.36	0.0	0.00000001	0.0736	0.0011	0.1071	0.0009	1.8221	0.0327	1.796	0.016 05	1.61	-3	
91500		80	28	15	0.35	0.7	0.11	0.0000573	0.0749	0.0008	0.1052	0.0015	1.8543	0.0241	1.796	0.015 06	1.64	2
91500		82	28	15	0.35	0.0	0.00000001	0.0759	0.0006	0.1080	0.0008	1.8746	0.0216	1.792	0.015 07	1.74	2	
91500		82	28	15	0.35	0.1	0.01	0.0000040	0.0766	0.0006	0.1078	0.0007	1.8937	0.0217	1.792	0.015 07	1.71	3
91500		80	28	15	0.35	0.0	0.00000001	0.0759	0.0005	0.1065	0.0008	1.8583	0.0198	1.771	0.014 06	1.76	2	
91500		81	28	15	0.36	0.0	0.00000001	0.0740	0.0007	0.1063	0.0010	1.8327	0.0233	1.797	0.015 05	1.65	2	
91500		81	28	15	0.35	0.0	0.00000039	0.0744	0.0005	0.1055	0.0005	1.8535	0.0195	1.806	0.015 05	1.75	-2	
91500		81	28	15	0.35	0.3	0.04	0.0000226	0.0735	0.0006	0.1057	0.0011	1.8145	0.0206	1.790	0.015 05	1.72	-3
91500		81	28	15	0.35	0.0	0.00000001	0.0750	0.0004	0.1069	0.0008	1.8469	0.0162	1.785	0.015 04	1.82	2	
91500		82	28	15	0.35	0.0	0.00000039	0.0750	0.0006	0.1056	0.0007	1.8385	0.0259	1.779	0.020 20	0.81	2	
91500		81	28	15	0.35	0.0	0.00000001	0.0758	0.0008	0.1086	0.0009	1.8327	0.0273	1.753	0.019 07	1.74	2	
91500		80	27	15	0.35	0.5	0.08	0.0000426	0.0744	0.0009	0.1050	0.0015	1.8644	0.0299	1.817	0.019 06	1.66	2
91500		81	28	15	0.35	0.0	0.00000000	0.0753	0.0006	0.1067	0.0008	1.8803	0.0270	1.810	0.020 21	0.81	2	
91500		81	28	15	0.35	0.5	0.07	0.0000373	0.0736	0.0009	0.1068	0.0015	1.7978	0.0307	1.773	0.020 20	0.67	-2
91500		82	28	15	0.35	0.3	0.05	0.0000271	0.0738	0.0008	0.1055	0.0011	1.8414	0.0289	1.809	0.020 21	0.74	-3



sample	analysis no.	grain no.	U ppm	Th ppm	Pb ppm	Th/U	<sup>204</sup> Pb/ <sup>238</sup> Pb ppb	<sup>206</sup> Pb/ <sup>238</sup> Pb (%)	<sup>206</sup> Pb/ <sup>238</sup> Pb	1σ	corrected ratios				ρ	Ages (Ma)				grain comment				
											<sup>207</sup> Pb/ <sup>235</sup> Pb	1σ	<sup>206</sup> Pb/ <sup>238</sup> Pb	1σ		<sup>206</sup> Pb/ <sup>238</sup> Pb	1σ	<sup>207</sup> Pb/ <sup>235</sup> Pb	1σ		<sup>206</sup> Pb/ <sup>238</sup> Pb	1σ	% disc	
91500		81	28	15	0.36	0.0	0.0000001	0.0000001	0.0741	0.0009	0.1073	0.0010	1.8001	0.0290	0.1763	1047	10	1046	10	1042	26	0		
		82	29	15	0.36	0.0	0.0000001	0.0000001	0.0740	0.0009	0.1081	0.0009	1.7955	0.0283	0.1759	1044	9	1044	10	1042	25	0		
		82	29	15	0.36	0.3	0.04	0.0000207	0.0747	0.0007	0.1082	0.0012	1.8439	0.0259	0.1799	1061	10	1061	9	1061	18	0		
		79	28	14	0.36	0.2	0.03	0.0000147	0.0749	0.0006	0.1097	0.0009	1.8427	0.0259	0.1783	1058	11	1061	9	1066	16	1		
		81	28	15	0.36	0.7	0.10	0.0000536	0.0766	0.0008	0.1061	0.0016	1.8613	0.0284	0.1782	1057	11	1075	10	1109	19	5		
		81	28	15	0.36	0.0	0.0000001	0.000000001	0.0741	0.0008	0.1087	0.0010	1.8234	0.0283	0.1784	1058	11	1054	10	1044	22	-1		
		83	29	15	0.36	0.0	0.0000001	0.000000001	0.0757	0.0007	0.1084	0.0011	1.8966	0.0288	0.1817	1076	11	1080	10	1087	19	1		
Session 1	temora	155	49	10	0.32	0.4	0.09	0.0000468	0.0559	0.0006	0.1007	0.0015	0.5057	0.0104	0.0656	0.0012	0.86	410	7	416	7	447	19	8
	temora	1821	863	131	0.49	0.5	0.01	0.0000050	0.0552	0.0001	0.1529	0.0009	0.5232	0.0093	0.0688	0.0012	0.99	429	7	427	6	419	6	-2
	temora	111	57	8	0.53	0.3	0.09	0.0000459	0.0531	0.0006	0.1647	0.0020	0.4936	0.0104	0.0674	0.0012	0.85	420	7	407	7	335	17	-25
	temora	77	22	5	0.30	0.1	0.02	0.0000118	0.0539	0.0010	0.0939	0.0013	0.4942	0.0130	0.0665	0.0012	0.69	415	7	408	9	365	41	-14
	temora	111	27	7	0.25	0.1	0.02	0.0000084	0.0539	0.0007	0.0794	0.0009	0.5001	0.0110	0.0673	0.0012	0.81	420	7	412	7	366	28	-15
	temora	104	29	7	0.29	0.0	0.0000002	0.000000441	0.0549	0.0010	0.0897	0.0014	0.5101	0.0102	0.0674	0.0006	0.45	421	4	419	7	407	39	-3
	temora	60	19	4	0.32	0.2	0.08	0.0000441	0.0532	0.0010	0.0969	0.0018	0.4980	0.0110	0.0679	0.0007	0.45	424	4	410	7	335	38	-26
	temora	124	56	9	0.46	0.0	0.0000001	0.000000001	0.0555	0.0008	0.1427	0.0013	0.5154	0.0090	0.0673	0.0007	0.62	420	4	422	6	432	31	3
	temora	119	35	8	0.30	0.2	0.07	0.0000352	0.0553	0.0006	0.0912	0.0023	0.5127	0.0080	0.0672	0.0007	0.69	419	4	420	5	425	21	1
	temora	181	91	13	0.51	0.0	0.01	0.0000041	0.0561	0.0006	0.1581	0.0009	0.5220	0.0075	0.0675	0.0008	0.62	421	4	427	5	456	24	8
	temora	104	48	7	0.47	0.3	0.11	0.0000563	0.0541	0.0008	0.1460	0.0020	0.4983	0.0087	0.0668	0.0007	0.57	417	4	411	6	374	27	-11
	temora	117	37	8	0.32	0.1	0.04	0.0000210	0.0562	0.0010	0.1013	0.0015	0.5160	0.0106	0.0666	0.0007	0.51	415	4	422	7	460	38	10
	temora	102	51	7	0.51	0.3	0.11	0.0000584	0.0551	0.0008	0.1572	0.0020	0.5097	0.0093	0.0671	0.0007	0.55	419	4	418	6	416	29	-1
	temora	105	33	7	0.32	0.2	0.08	0.0000409	0.0548	0.0007	0.0988	0.0015	0.5064	0.0084	0.0670	0.0007	0.59	418	4	416	6	403	26	-4
	temora	110	32	7	0.30	0.0	0.01	0.0000073	0.0557	0.0008	0.0923	0.0011	0.5143	0.0096	0.0670	0.0008	0.66	418	5	421	6	440	30	5
	temora	131	61	9	0.48	0.0	0.0000001	0.000000001	0.0561	0.0006	0.1475	0.0014	0.5208	0.0077	0.0673	0.0007	0.66	420	4	426	5	457	24	8
	temora	585	298	41	0.52	0.9	0.05	0.0000270	0.0555	0.0003	0.1631	0.0008	0.5089	0.0057	0.0665	0.0007	0.89	415	4	418	4	432	10	4
	temora	609	315	43	0.53	0.2	0.01	0.0000050	0.0556	0.0004	0.1662	0.0009	0.5138	0.0064	0.0670	0.0007	0.81	418	4	421	4	437	16	4
	temora	632	327	45	0.53	0.7	0.03	0.0000183	0.0547	0.0005	0.1646	0.0006	0.5085	0.0068	0.0670	0.0007	0.76	421	4	417	5	388	19	-6
	temora	672	352	48	0.54	0.2	0.01	0.0000046	0.0550	0.0003	0.1669	0.0007	0.5076	0.0058	0.0670	0.0007	0.88	418	4	417	4	411	12	-2
temora	61	28	4	0.47	0.3	0.17	0.0000890	0.0529	0.0014	0.1449	0.0032	0.4741	0.0138	0.0650	0.0008	0.42	406	5	394	9	325	49	-25	
temora	153	70	11	0.47	0.6	0.12	0.0000641	0.0530	0.0007	0.1443	0.0023	0.4877	0.0083	0.0667	0.0008	0.67	416	5	403	6	329	22	-27	
temora	100	27	7	0.28	0.7	0.23	0.0001222	0.0537	0.0009	0.0835	0.0030	0.4997	0.0096	0.0675	0.0008	0.50	421	4	411	6	356	22	-18	
temora	143	66	10	0.47	0.0	0.000000001	0.000000001	0.0555	0.0008	0.1434	0.0015	0.5188	0.0089	0.0678	0.0008	0.51	423	4	424	6	433	33	2	
temora	91	28	6	0.32	0.5	0.16	0.0000864	0.0552	0.0011	0.0997	0.0024	0.5152	0.0116	0.0676	0.0007	0.43	422	4	422	8	422	37	0	
temora	103	33	7	0.32	0.3	0.10	0.0000558	0.0549	0.0010	0.0982	0.0019	0.5133	0.0108	0.0678	0.0007	0.47	423	4	421	7	408	36	-4	
temora	70	25	5	0.36	0.0	0.00000002	0.000000001	0.0542	0.0007	0.1023	0.0014	0.4948	0.0088	0.0663	0.0007	0.63	414	5	408	6	377	31	-10	
temora	63	23	4	0.38	0.6	0.31	0.0001672	0.0535	0.0016	0.1164	0.0042	0.5041	0.0158	0.0683	0.0008	0.36	426	5	415	11	351	48	-21	
temora	53	17	4	0.34	0.1	0.04	0.0000191	0.0560	0.0009	0.1035	0.0022	0.5157	0.0095	0.0668	0.0006	0.53	417	4	422	6	452	31	8	
temora	82	39	6	0.49	0.0	0.00000002	0.000000001	0.0540	0.0008	0.1507	0.0022	0.4983	0.0098	0.0670	0.0008	0.60	418	5	411	7	370	35	-13	
temora	106	51	7	0.50	0.2	0.06	0.0000299	0.0552	0.0010	0.1578	0.0022	0.4939	0.0102	0.0649	0.0006	0.48	405	4	408	7	419	38	3	
temora	110	33	7	0.31	0.2	0.06	0.0000337	0.0540	0.0008	0.0964	0.0015	0.4855	0.0086	0.0652	0.0006	0.47	407	3	402	6	371	31	-10	
temora	136	71	10	0.54	0.1	0.02	0.0000083	0.0559	0.0008	0.1685	0.0018	0.5190	0.0087	0.0673	0.0005	0.43	420	3	424	6	450	32	7	







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grain no.	SQA/03 - SQA/03 - SQA/03 - SQA/03 - SQA/03 - SQA/03 - SQA/03 - SQA/03 - SQA/03 - SQA/03 -										L2-04									
	8.13	8.14x	9	9	9	9	9	9	9	9	10.20	10.20	10.21	10.21	10.21	10.21	10.21	10.21	10.21	10.21
Si	140230	237	116	85	495	140	136	109	441	3104	225	369	264	808	1016	616	325	209	17024	196
P	558	237	116	85	495	140	136	109	441	3104	225	369	264	808	1016	616	325	209	17024	196
Ca	7	1513	1	1	8	0	20	1	21	5328	2	8	1	1	10	5	13	23900	3	1
Ti	1	1513	12	12	175	2	13	10	1593	1166	1071	1490	541	2192	1318	1827	705	304	1634	273
V	2721	487	410	217	1186	381	243	458	10	10	2	13	3	18	5	11	4	1	2	1
Nb	547490	589050	553320	547290	560340	549580	561360	568190	546870	522520	530170	540700	534570	528280	526810	531710	525300	526980	507440	536280
Zr	0.9	3.0	0.2	0.1	2.0	0.2	0.1	0.1	12.7	1.1	0.1	0.3	0.1	0.1	0.1	1.9	0.2	0.3	0.8	0.0
Ba	3.0	0.0	0.0	0.0	8.7	0.0	2.0	0.0	12.1	85.2	1.0	0.7	0.0	0.1	0.1	7.7	0.0	0.0	239.6	0.0
La	120.7	21.9	13.6	10.6	74.9	12.3	14.1	10.0	116.7	269.2	39.1	81.5	23.9	88.4	22.4	88.6	27.4	14.6	611.0	10.3
Ce	3.0	0.2	0.1	0.1	6.0	0.1	1.2	0.1	7.0	30.6	1.1	0.6	0.1	0.3	0.1	6.8	0.1	0.1	74.5	0.0
Pr	26.3	7.7	4.6	1.1	36.2	1.0	9.0	0.1	43.9	8.8	0.0	1.5	0.6	2.0	0.8	48.4	1.5	0.8	372.9	0.5
Nd	35.2	21.7	12.6	1.1	51.3	1.1	11.3	0.1	57.4	12.7	0.1	3.0	0.1	1.1	0.1	64.1	0.1	0.1	511.1	0.4
Eu	3.5	1.0	1.2	0.5	2.7	0.7	0.8	1.2	3.8	2.5	2.5	1.3	0.7	2.2	1.2	4.4	0.7	0.4	9.1	0.4
Gd	92	14	12	5	30	8	13	52	49	35	28	11	62	31	55	12	6	111	6	21
Tb	29	5	4	2	9	3	2	4	16	12	10	11	4	21	11	16	5	2	22	2
Dy	327	55	41	20	117	37	23	51	187	129	119	151	50	257	140	180	60	26	206	25
Ho	113	20	14	7	43	13	9	18	65	45	43	59	20	90	52	63	24	10	63	10
Er	527	104	73	37	220	70	46	90	297	217	206	302	105	404	251	290	130	52	269	47
Tm	107	23	16	0	51	15	11	19	61	46	42	69	25	82	53	58	30	12	53	11
Yb	61	10	6	0	20	5	3	5	18	14	10	16	6	25	19	18	8	3	19	3
Lu	190	46	37	24	96	32	24	39	109	84	79	137	56	132	95	121	69	28	88	24
Hf	11089	11835	10054	10693	12569	10236	10701	10642	12277	12876	10835	13139	10467	11722	11412	12115	9845	10074	8779	9837
Th	774	75	82	36	140	34	36	55	325	250	160	341	86	742	96	251	109	46	164	30
U	952	131	83	58	468	60	60	76	537	538	224	767	159	987	283	548	190	85	165	57
La	12.99	36.39	0.20	0.10	37.05	0.20	8.43	0.19	51.58	383.02	4.16	2.90	0.13	0.33	0.22	32.93	0.09	0.11	1020.66	0.09
Ce	200.17	124.19	20.34	17.60	124.19	20.34	23.32	16.66	196.75	448.34	64.86	135.16	39.64	146.58	37.14	146.82	45.37	24.17	1012.95	171.15
Nd	58.02	3.76	5.65	2.38	79.97	2.15	19.97	4.07	79.57	317.89	19.49	10.99	3.24	14.61	4.46	107.08	3.34	1.71	824.31	1.10
Sm	151	18	22	9	90	12	21	19	117	216	50	28	14	73	32	169	14	8	168	8
Eu	62	18	22	9	47	12	14	21	65	45	44	23	13	40	21	79	13	6	168	8
Gd	467	72	60	27	153	38	39	67	265	249	176	141	54	315	155	279	61	30	564	31
Tb	792	126	98	51	256	77	57	114	449	331	282	295	106	584	305	438	132	584	31	54
Dy	1346	225	169	84	483	151	97	208	769	531	491	621	205	1057	740	245	108	849	104	173
Ho	2028	364	258	134	778	238	159	317	1165	806	770	1062	356	1621	936	1134	430	183	1140	173
Er	3318	652	461	234	1381	438	287	565	1867	1363	1293	1902	660	2545	1580	1825	817	329	1694	297
Tm	4441	937	662	405	2100	630	451	794	2502	1894	1754	2841	1038	3370	2202	2388	1239	507	2191	465
Yb	7813	1616	1038	574	3544	1038	630	1038	3544	2202	1894	2841	1038	3370	2202	2388	1239	507	2191	465
Lu	7813	1616	1038	574	3544	1038	630	1038	3544	2202	1894	2841	1038	3370	2202	2388	1239	507	2191	465
Hf	1096250	1137981	965731	1028942	125692	984231	1028942	1028942	125692	984231	1028942	125692	984231	1028942	125692	984231	1028942	125692	984231	1028942
Th	313	30	33	15	57	14	14	22	1180481	1238077	85	138	35	300	39	102	44	18	66	12
U	117553	16199	10248	7174	7936	9405	132	101	1238077	27654	19690	94706	19690	1238077	34905	67685	23454	10497	20370.01	6978
ThU	0.8	0.6	1.0	0.6	0.3	0.6	0.6	0.7	0.6	0.5	0.7	0.4	0.5	0.7	0.3	0.5	0.6	0.5	1.0	0.5
Yb(n)/La(n)	382	1386	4343	5776	69	3998	69	5116	59	6	512	1236	10329	11393	11890	84	18453	5964	2	6059
Yb(n)/Gd(n)	10.9	15.4	14.4	21.2	16.7	21.3	14.9	14.8	11.5	9.2	12.1	25.3	25.5	12.1	16.7	10.0	27.2	22.4	44	18.1
Eu/Eu*	0.2	0.5	0.6	0.7	0.4	0.6	0.4	0.6	0.4	0.5	0.3	0.5	0.3	0.5	0.3	0.4	0.5	0.4	0.5	0.3
Ce/Ce*	26.9	36.5	61.8	61.8	25.5	57.3	2.2	33.7	3.1	1.3	9.0	30.7	111.9	130.4	67.4	2.9	133.7	86.9	1.1	91.1
HfO <sub>2</sub> [wt%]	1.3	1.4	1.2	1.3	1.5	1.2	1.3	1.3	1.4	1.5	1.3	1.3	1.2	1.4	1.3	1.4	1.2	1.2	1.0	1.2
comment	rejected, crack	rejected, crack	rejected, crack	rejected, crack	rejected, crack	rejected, crack	rejected, crack	rejected, crack	rejected, crack	rejected, crack	rejected, crack	rejected, crack	rejected, crack	rejected, crack	rejected, crack	rejected, crack	rejected, crack	rejected, crack	rejected, crack	rejected, crack
grain area	c1	c1	c2a	c2b	c2	rm	c2	c1	rm	rm	c1	rm	c1	c2a	c2b	rm	c2	rm	c1	rm

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L3																			
SA04/12 - SA04/05 - SA04/05 - SA04/05 - SA04/05 - SA04/05 - SA04/05 - SA04/05 - SA04/05 - SA04/05 - SA04/05 - SA04/05 - SA04/05 - SA04/05 - SA04/05 - SA04/05 - SA04/05 - SA04/05 - SA04/05 - SA04/05 -																			
14,35 15,37 15,38 11,26 21,40 21,41 14,27 9,16 9,17 25,49 25,50 18,34 18,35 28,56 10,18 4,7 5,9 11,21 11,22 24,48																			
grain no.	14	15	15	11	21	21	14	9	25	25	18	18	28	10	4	5	11	11	24
Si	140230	140230	140230	140230	140230	140230	140230	140230	140230	140230	140230	140230	140230	140230	140230	140230	140230	140230	140230
P	446	1142	575	434	914	697	388	429	681	365	370	301	418	419	680	615	1643	659	612
Ca	17	8	16	24	9	13	6	4	2	2	1	2	1	1	1	2	3	11	4
Ti	20	4	7	6	7	6	11	9	6	8	8	7	1	2	5	7	3	9	6
Y	2704	1866	2030	1278	2457	1425	1824	1555	1421	1197	1795	2371	1482	2091	1433	1937	3185	1795	1986
Nb	54670	507090	517550	544530	551280	530840	550400	549390	557910	547050	555550	551730	550560	559620	562700	544150	528020	531060	536490
Ba	0,3	0,2	0,1	0,2	1,4	1,3	0,5	0,4	0,1	0,2	0,0	0,1	0,2	0,1	0,0	0,4	0,0	0,8	0,1
La	5,1	0,1	0,8	0,2	3,0	13,5	4,0	0,7	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,5	1,1	0,4	0,6
Ce	118,3	47,5	77,4	57,9	98,8	173,5	79,4	82,4	40,5	56,9	73,4	63,0	63,0	83,1	41,2	49,7	64,9	94,9	83,3
Pr	4,8	0,2	0,3	0,4	1,9	7,3	1,7	0,7	0,2	0,3	0,2	0,9	0,4	0,5	0,2	0,7	0,9	0,4	0,8
Nd	34,7	3,1	3,7	4,8	14,0	34,6	13,5	1,6	3,5	4,7	16,6	15,1	9,3	5,3	4,0	9,3	6,6	6,3	8,7
Sm	16	1,1	1,2	1,7	11,0	26,7	11,7	0,9	4,8	6,3	24,3	18,4	10,3	6,4	4,5	11,2	8,3	11,2	10,0
Eu	4,6	1,2	1,1	1,7	3,1	2,1	2,4	2,4	1,8	1,4	1,6	4,5	2,4	2,7	1,8	3,1	1,0	2,4	0,3
Gd	101	40	51	36	68	40	47	47	36	35	42	88	41	51	37	58	66	51	53
Tb	31	15	18	12	23	13	15	16	13	11	14	27	15	19	13	18	25	17	18
Dy	337	190	212	142	278	154	187	184	158	137	185	301	176	235	162	211	320	198	210
Ho	110	71	78	50	99	56	72	64	58	50	70	100	60	86	60	75	123	71	76
Er	473	343	362	227	470	268	368	292	294	230	359	456	293	414	290	333	579	316	344
Tm	94	73	75	49	98	57	79	59	61	48	77	88	59	84	62	69	123	65	71
Yb	153	104	109	69	179	104	151	103	112	82	145	149	95	147	114	123	215	109	124
Lu	11348	10217	11494	11241	10972	11034	10647	11177	10830	11123	11131	10882	10683	10516	11110	10356	12269	10299	11407
Hf	531	363	484	432	798	275	336	940	275	483	357	477	710	540	281	325	736	1334	718
Th	725	931	1394	661	1439	778	708	1077	595	699	771	648	778	696	609	509	2295	1308	1195
La	21,76	0,52	3,27	0,73	12,79	57,52	16,97	2,96	0,31	0,28	0,28	0,51	0,51	1,46	0,31	2,04	4,90	1,59	2,52
Ce	196,10	78,79	125,32	95,91	163,78	287,67	131,59	136,62	67,20	97,70	121,61	104,41	104,45	137,89	68,24	82,34	107,66	157,31	154,64
Nd	76,83	6,96	8,12	10,57	30,93	76,49	29,87	16,73	7,64	10,46	10,10	33,39	11,83	11,67	8,79	20,52	14,62	13,99	19,22
Sm	215	44	50	48	95	107	40	65	43	43	58	124	64	64	64	76	64	68	68
Eu	63	21	19	30	55	44	43	43	32	25	29	80	43	48	33	56	18	43	36
Gd	515	204	259	183	344	205	238	238	181	179	214	446	210	261	186	294	336	259	272
Tb	841	421	497	336	631	357	421	442	360	310	385	737	418	524	364	509	690	470	496
Dy	1388	782	874	585	1146	635	769	758	650	565	763	1240	723	968	667	869	1320	818	866
Ho	1978	1276	1401	898	1783	1008	1303	1158	1052	891	1260	1792	1075	1539	1073	1348	2209	1280	1367
Er	2974	2158	2276	1426	2958	1696	2317	1839	1787	1445	2261	2867	1844	2506	1826	2099	3645	1986	2164
Tm	3890	3007	3099	2014	4066	2351	3276	2448	2520	1980	3173	3689	2399	3455	2572	2881	5057	2885	2949
Yb	4866	3772	3846	2456	4946	2772	4066	2956	2456	1980	3173	3689	2399	3455	2572	2881	5057	2885	2949
Lu	6307	5693	5498	3640	7349	4279	6221	4244	4699	3398	5992	6127	5928	6960	4692	5056	8841	4503	5085
Hf	1091154	982404	1105192	1090865	1055000	1060982	1022750	1074712	1050962	1069519	1056962	1027212	1011154	1064269	985769	1173842	990288	1096827	914846
Th	215	147	196	175	323	111	136	380	111	195	144	193	298	219	114	132	298	540	291
U	89553	114983	172111	81602	177642	96043	87390	132951	73505	86252	95185	79944	96109	85873	75167	62793	283321	161531	147531
Th/U	0,7	0,4	0,5	0,9	0,6	0,4	0,5	0,9	0,5	0,7	0,5	0,7	0,9	0,8	0,5	0,6	0,3	1,0	0,6
Yb(n)/La(n)	199	6765	1069	3133	380	48	234	937	9668	13467	8258	5316	2747	9851	1626	1201	1926	1339	4776
Yb(n)/Gd(n)	8,4	17,3	13,5	12,6	14,2	13	16,7	11,7	12,5	17,9	9,4	13,0	15,3	16,4	11,3	17,5	11,9	12,4	17,5
Eu/Eu*	0,2	0,2	0,2	0,3	0,3	0,3	0,3	0,3	0,3	0,3	0,3	0,3	0,4	0,4	0,4	0,4	0,1	0,3	0,4
Ce/Ce*	5,7	73,6	39,7	55,5	9,8	4,2	7,3	28,5	90,5	110,6	141,0	44,8	72,1	50,3	92,1	20,1	15,1	58,2	31,9
HfO <sub>2</sub> [wt%]	1,3	1,2	1,4	1,3	1,3	1,3	1,3	1,3	1,3	1,3	1,3	1,3	1,3	1,2	1,3	1,2	1,4	1,2	1,3
comment													cycle 5-10						rim
grain area	c1	c1	c2	c2	c2	rim	rim	c2a	c2b	c2b	c2a	c2a	c2b	rim	c1	c1+c2	c1	c2a	c2b
																			rim

Standards															
grain no.	91500- oct06-2	91500- oct06-3	91500- oct06-4	91500- oct06-5	91500- oct06-6	91500- oct06-7	91500- oct06-8	91500- oct06-9							
Si	140230	140230	140230	140230	140230	140230	140230	140230							
P	262.16	28.843	25.951	23	21.612	25.393	26.663	24.668							
Ca	3	10	9	5	7	8	6	11							
Ti	5	15	14	4	13	14	14	13							
V	1619	131	140	142	141	143	141	144							
Nb	515150	520500	528980	536940	545560	547760	538050	522670							
Zr	0	0	0	0	0	0	0	0							
Ba	0	0	0	0	0	0	0	0							
La	0	0	0	0	0	0	0	0							
Ce	26.6	3	3.1	3.4	3.2	2.9	3.3	3.1							
Pr	0.3	0	0.0	0.0	0.0	0.0	0.0	0.0							
Nd	5.6	0	0.3	0.3	0.2	0.2	0.4	0.3							
Sm	0.4	0	0.4	0.3	0.5	0.4	0.4	0.5							
Eu	0.3	0	0.3	0.2	0.2	0.3	0.2	0.2							
Gd	37.4	2	2.0	2.7	2.4	2.7	2.2	2.4							
Tb	11.7	1	1.0	0.9	0.9	1.0	1.0	0.9							
Dy	136	12	12	12	13	13	12	11							
Ho	50	5	5	5	5	5	5	5							
Er	258	27	28	30	29	28	28	27							
Tm	59	7	7	7	7	7	7	8							
Yb	514	61	65	68	69	66	65	62							
Lu	121	15	16	17	16	17	16	15							
Hf	18270	6273	6473	6812	6944	6962	6659	6869							
Th	981	25	28	30	29	29	29	26							
U	2963	79	85	91	92	93	91	94							
La	0.12	0.12	0.05	0.05	0.03	0.05	0.06	0.03							
Ce	44.02	5.43	5.16	5.58	5.25	4.87	5.45	5.17							
Pr	12.45	0.3	0.14	0.15	0.16	0.15	0.15	0.15							
Nd	12.45	0.49	0.72	0.71	0.46	0.54	0.81	1.01							
Sm	64	3	2	2	3	3	3	3							
Eu	6	4	4	3	4	5	4	4							
Gd	190	11	10	14	12	14	11	12							
Tb	323	23	27	26	26	25	28	27							
Dy	559.2089	48.57437	48	50	52	52	49	51							
Ho	907	86	87	94	92	91	89	95							
Er	1623	168	179	189	184	178	177	179							
Tm	2445	284	299	303	287	309	306	315							
Yb	3160.165	378.2892	397	419	425	405	402	403							
Lu	4987.243	615.3498	657	687	674	686	668	709							
Hf	1756731	603173	622385	655010	667673	669375	640240	669490							
Th	397.3	10.0	11.4	12.2	11.9	11.9	12.0	12.0							
U	385851.85	9740.74	10481.48	11246.91	11417.65	11423.46	11210.49	11665.93							
Th/U	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3							
Yb(n)/La(n)	26852	3208	8504	7664	8188	6541	14697	7							
Yb(n)/Gd(n)	16.6	35.1	39.2	34.7	30.0	36.1	33.4	20.0							
Eu/Er	0.1	0.7	0.9	0.6	0.7	0.8	0.7	0.6							
Ce/Ce*	68.3	35.8	41.1	43.5	72.3	87.2	41.0	65.5							
HfO <sub>2</sub> [wt%]	2.2	0.7	0.8	0.8	0.8	0.8	0.8	0.8							
comment															
grain area															

Appendix 2e

Zircon oxygen isotope data of the Etive pluton and average values of bracketing zircon standard 91500

analyses no.	grain no.	$^{18}\text{O}/^{16}\text{O}$ (measured)	2SD	1 s.e.m.	$^{18}\text{O}/^{16}\text{O}$ (drift corrected)	$\delta^{18}\text{O}$ [‰] VSMOW	2SD	1 s.e.m.	n	grain area	comment
Session 2 (24.04.2006)											
91500/1 - 31-40		0.0020128	0.0000015	0.0000002		9.77	0.7	0.112	10		
91500/1 - 41-45, 47-50		0.0020121	0.0000018	0.0000003		9.47	0.9	0.142	9		
91500/2 - 1-10		0.0020133	0.0000012	0.0000002		10.04	0.6	0.094	10		
91500/2 - 11-20		0.0020131	0.0000017	0.0000003		9.93	0.8	0.128	10		
91500/2 - 21-30		0.0020134	0.0000018	0.0000003		10.11	0.8	0.131	10		
91500/1 - 51-60		0.0020128	0.0000011	0.0000002		9.82	0.5	0.084	10		
MO	SA05-20_1a	1	0.0020019	0.0000004		4.4		0.080		c2a	rejected, scratch
	SA05-20_2a	2	0.0020022	0.0000002		4.5		0.044		c1	rejected, crack
	91500/1 - 61, 63-70		0.0020129	0.0000021	0.0000003	9.85	1.0	0.153	9		
Session 3 (25.04.2006)											
91500/14 - 52-61		0.0020157	0.0000007	0.0000001		9.74	0.4	0.055	10		
91500/1 - 1-10		0.0020162	0.0000014	0.0000002		9.98	0.7	0.109	10		
St-01	SA05/01 - 1a	1	0.0020087	0.0000002		6.3		0.051		c1	rejected, crack
	SA05/01 - 2a	2	0.0020108	0.0000001		7.3		0.042		c2	rejected, grain altered
	SA05/01 - 2b	2	0.0020129	0.0000002		8.3		0.078		c2+rim	rejected, crack
	SA05/01 - 3a	3	0.0020100	0.0000002		6.9		0.085		c2	rejected, crack
	SA05/01 - 4a	4	0.0020111	0.0000003		7.4		0.112		c1	
	SA05/01 - 6a	6	0.0020102	0.0000002		7.0		0.060		c2a	
	SA05/01 - 5b	5	0.0020110	0.0000001		7.4		0.054		c1	
	SA05/01 - 5c	5	0.0020108	0.0000003		7.3		0.110		rim	
	SA05/01 - 7a	7	0.0020106	0.0000003		7.2		0.091		c2	
	SA05/01 - 8a	8	0.0020104	0.0000002		7.1		0.078		c1	
Session 4 (25.04.2006)											
91500/1 - 11-15, 17-20		0.0020170	0.0000007	0.0000001		9.91	0.4	0.061	9		
SA05/01 - 8b	8	0.0020094	0.0000002			6.1		0.072		c2	rejected, crack
SA05/01 - 9a	9	0.0020111	0.0000003			7.0		0.106		c1	
SA05/01 - 11a	11	0.0020102	0.0000002			6.6		0.058		c2	rejected, crack
SA05/01 - 11c	11	0.0020101	0.0000002			6.5		0.052		rim	
SA05/01 - 12a	12	0.0020113	0.0000003			7.1		0.100		c2	
SA05/01 - 13a	13	0.0020110	0.0000002			6.9		0.072		c2	
SA05/01 - 13b	13	0.0020098	0.0000002			6.3		0.071		rim	
SA05/01 - 14a	14	0.0020111	0.0000003			7.0		0.101		rim	
SA05/01 - 15a	15	0.0020104	0.0000001			6.6		0.040		r1	
SA05/01 - 15b	15	0.0020119	0.0000003			7.4		0.113		r2	rejected, crack
91500/1 - 21b, 22, 24-30		0.0020169	0.0000007	0.0000001		9.88	0.4	0.060	9		
SA05/01 - 16a	16	0.0020104	0.0000002			6.63		0.068		c2	rejected, correction on position of secondary ion beam anomalously large
SA05/01 - 17a	17	0.0020102	0.0000002			6.5		0.054		c2	rejected, crack
SA05/01 - 18a	18	0.0020104	0.0000002			6.7		0.071		c2a	
SA05/01 - 18b	18	0.0020103	0.0000003			6.6		0.086		c2b	
SA05/01 - 19c	19	0.0020102	0.0000002			6.6		0.081		c1	rejected, crack
SA05/01 - 19b	19	0.0020101	0.0000001			6.5		0.040		rim	
SA05/01 - 20a	20	0.0020113	0.0000002			7.1		0.060		c2	
St-05	SA05/05 - 1a	1	0.0020100	0.0000002		6.4		0.053		c1	
	SA05/05 - 2a	2	0.0020112	0.0000002		7.1		0.081		rim	
	SA05/05 - 3b	3	0.0020104	0.0000003		6.6		0.095		rim	
	SA05/05 - 4a	4	0.0020116	0.0000002		7.2		0.072		c2	
	SA05/05 - 4b	4	0.0020072	0.0000004		5.0		0.089		rim	rejected, grain altered
	SA05/05 - 5a	5	0.0020111	0.0000003		7.0		0.121		rim	rejected, crack
	SA05/05 - 6a	6	0.0020102	0.0000003		6.5		0.099		rim	
	SA05/05 - 7a	7	0.0020107	0.0000002		6.8		0.056		rim	
	SA05/05 - 8a	8	0.0020101	0.0000002		6.5		0.070		c1	rejected, crack
	SA05/05 - 9a	9	0.0020109	0.0000003		6.9		0.112		c2	
	SA05/05 - 10a	10	0.0020113	0.0000001		7.1		0.043		c2	
	SA05/05 - 10b	10	0.0020112	0.0000002		7.0		0.080		rim	
	SA05/05 - 11a	11	0.0020192	0.0000003		11.0		0.144		c2a	analytical problem
	91500/1 - 36-40		0.0020165	0.0000005	0.0000001	9.67	0.3	0.059	5		
	91500/1 - 41-45		0.0020170	0.0000008	0.0000002	9.92	0.4	0.089	5		
	SA05/05 - 11b	11	0.0020113	0.0000003		7.1		0.107		rim	
	SA05/05 - 11c	11	0.0020126	0.0000002		7.7		0.090		c2b	
	SA05/05 - 12a	12	0.0020101	0.0000003		6.5		0.088		c2	rejected, crack
	SA05/05 - 13a	13	0.0020107	0.0000002		6.8		0.071		c2a	
	SA05/05 - 13b	13	0.0020112	0.0000001		7.1		0.040		c2b	rejected, crack
	SA05/05 - 14c	14	0.0020114	0.0000003		7.1		0.104		r1a	
	SA05/05 - 14b	14	0.0020104	0.0000002		6.7		0.074		r1b	
	SA05/05 - 15a	15	0.0020110	0.0000002		6.9		0.081		c1	rejected, crack
	SA05/05 - 15b	15	0.0020114	0.0000002		7.2		0.071		rim	
	SA05/05 - 16a	16	0.0020099	0.0000003		6.4		0.090		c2	
	SA05/05 - 23a	23	0.0020106	0.0000002		6.8		0.067		c2	
	SA05/05 - 17a	17	0.0020106	0.0000001		6.7		0.030		rim	
	SA05/05 - 18a	18	0.0020105	0.0000003		6.7		0.104		c1	
	SA05/05 - 18b	18	0.0020103	0.0000003		6.6		0.094		c2	
	SA05/05 - 19a	19	0.0020106	0.0000003		6.8		0.094		c1	
	SA05/05 - 19b	19	0.0020104	0.0000002		6.7		0.053		c2	
	SA05/05 - 20a	20	0.0020112	0.0000003		7.1		0.091		rim	



**Appendix 2e**  
**Zircon oxygen isotope data of the Etive pluton and average values of bracketing zircon standard 91500**

analyses no.	grain no.	$^{18}\text{O}/^{16}\text{O}$ (measured)	2SD	1 s.e.m.	$^{18}\text{O}/^{16}\text{O}$ (drift corrected)	$\delta^{18}\text{O}$ [‰] VSMOW	2SD	1 s.e.m.	n	grain area	comment
<b>Session 5 (25.04.2006)</b>											
91500/1 - 46-50		0.0020157	0.0000009	0.0000002		9.86	0.4	0.100	5		
SA05/05 - 21a	21	0.0019430		0.0000012		-26.3		-1.643		c2a	instrument failure
SA05/05 - 21b	21	0.0019749		0.0000007		-10.5		-0.382		c2b	instrument failure
SA05/05 - 22a	22	0.0019254		0.0000007		-35.1		-1.188		rim	instrument failure
<b>Session 6 (12.06.2006)</b>											
Mount4/91500 - 1-3, 5-10		0.0020222	0.0000008	0.0000001	0.0020222	9.85	0.395	0.066	9		
<b>Cr-15</b>	<b>SA05/15 - 2a</b>	2	0.0020148	0.0000003		6.2		0.098		c1	
	SA05/15 - 3a	3	0.0020153	0.0000003		6.4		0.101		c2	
	SA05/15 - 3b	3	0.0020152	0.0000002		6.3		0.065		c1	
	SA05/15 - 4a	4	0.0020164	0.0000002		7.0		0.061		inh1	inherited
	SA05/15 - 4b	4	0.0020140	0.0000002		5.8		0.046		rim	
	SA05/15 - 4c	4	0.0020165	0.0000005		7.0		0.159		inh2	inherited
	SA05/15 - 8a	8	0.0020143	0.0000004		5.9		0.107		inh1	inherited
	SA05/15 - 8b	8	0.0020153	0.0000003		6.4		0.080		rim	rejected, crack
	SA05/15 - 9a	9	0.0020131			5.3				c2	rejected, > 20 % discordant
	SA05/15 - 11a	11	0.0020151	0.0000002		6.3		0.051		c2a	
			0.0000005					0.166			
Mount4/91500 - 12-15		0.0020225	0.0000006	0.0000001	0.0020223	9.93	0.3	0.069	4		
SA05/15 - 11b	11	0.0020156	0.0000003			6.5		0.113		c2b	
SA05/15 - 15a	15	0.0020149	0.0000004			6.2		0.130		c2a	
SA05/15 - 15b	15	0.0020133	0.0000002			5.4		0.041		c2b	rejected, crack
SA05/15 - 19a	19	0.0020163	0.0000005			6.9		0.157		c1	
SA05/15 - 19b	19	0.0020153	0.0000003			6.4		0.095		c2	
SA05/15 - 22a	22	0.0020161	0.0000006			6.8		0.201		c1	
SA05/15 - 22b	22	0.0020148	0.0000003			6.1		0.099		c2	
SA05/15 - 25a	25	0.0020152	0.0000003			6.3		0.099		c1	rejected, crack
SA05/15 - 25b	25	0.0020140	0.0000003			5.7		0.088		c2	
SA05/15 - 26a	26	0.0020144	0.0000004			5.9		0.127		c1	
Mount4/91500 - 16-20		0.0020223	0.0000007	0.0000002	0.0020224	9.79	0.4	0.079	5		
SA05/15 - 26b	26	0.0020141	0.0000005			5.7		0.129		c2	rejected, correction on position of secondary ion beam anomalously large
SA05/15 - 29a	29	0.0020133	0.0000004			5.3		0.096		c2	
SA05/15 - 29b	29	0.0020142	0.0000004			5.8		0.108		rim	
SA05/15 - 1a	1	0.0020149	0.0000004			6.1		0.127		c1	rejected, correction on position of secondary ion beam anomalously large
SA05/15 - 5a	5	0.0020151	0.0000003			6.2		0.108		c1	rejected, crack
SA05/15 - 5b	5	0.0020149	0.0000005			6.1		0.144		rim	
<b>Cr-26</b>	<b>SA05/26 - 1b</b>	1	0.0020145	0.0000002		5.9		0.064		rim	rejected, > 20 % discordant
	SA05/26 - 1a	1	0.0020152	0.0000003		6.3		0.078		c1+rim	
	SA05/26 - 2a	2	0.0020151	0.0000002		6.2		0.056		c1	
	SA05/26 - 2b	2	0.0020147	0.0000002		6.0		0.067		rim	
Mount4/91500 - 21-25		0.0020227	0.0000009	0.0000002	0.0020225	9.94	0.5	0.103	5		
SA05/26 - 3a	3	0.0020146	0.0000005			5.9		0.135		c2a	rejected, > 20 % discordant
SA05/26 - 3b	3	0.0020145	0.0000003			5.9		0.089		c2b	
SA05/26 - 5a	5	0.0020139	0.0000005			5.6		0.138		c1	
SA05/26 - 6a	6	0.0020149	0.0000004			6.1		0.127		c1	
SA05/26 - 6b	6	0.0020157	0.0000004			6.5		0.117		c2	
SA05/26 - 7a	7	0.0020164	0.0000006			6.8		0.200		c2a	
SA05/26 - 7b	7	0.0020162	0.0000002			6.7		0.071		c2b	
SA05/26 - 8a	8	0.0020150	0.0000004			6.1		0.134		c2	
SA05/26 - 8b	8	0.0020135	0.0000005			5.4		0.141		rim	rejected, correction on position of secondary ion beam anomalously large
SA05/26 - 10a	10	0.0020147	0.0000003			6.0		0.101		c2	rejected, crack
Mount4/91500 - 27, 28, 30		0.0020224	0.0000001	0.0000000	0.0020226	9.79	0.1	0.017	3		
<b>Session 7 (12.06.2006)</b>											
Mount4/91500 - 31-35		0.0020231	0.0000008	0.0000002		9.89	0.4	0.089	5		
SA05/26 - 11b.2	11	0.0020168	0.0000002			6.8		0.063		c2b	
SA05/26 - 11b	11	NaN									analytical problem
SA05/26 - 11a	11	0.0020163	0.0000003			6.5		0.110		c2a	
SA05/26 - 12a	12	0.0020185	0.0000003			7.6		0.108		c2b	
SA05/26 - 12b	12	0.0020156	0.0000003			6.2		0.097		c2c	rejected, correction on position of secondary ion beam anomalously large
SA05/26 - 12c	12	0.0020181	0.0000002			7.4		0.090		c2a	rejected, correction on position of secondary ion beam anomalously large
SA05/26 - 13a	13	0.0020174	0.0000004			7.1		0.132		c1	rejected, crack
SA05/26 - 13b	13	0.0020153	0.0000002			6.0		0.054		c2	
SA05/26 - 14a	14	0.0020161	0.0000003			6.4		0.104		c1	
SA05/26 - 14b	14	0.0020158	0.0000004			6.3		0.115		c2	
Mount4/91500 - 36-40		0.0020231	0.0000007	0.0000002		9.90	0.3	0.075	5		
SA05/26 - 15b	15	0.0020171	0.0000004			6.9		0.151		r1a	rejected, correction on position of secondary ion beam anomalously large
SA05/26 - 15c	15	0.0020161	0.0000002			6.4		0.056		r1b	rejected, correction on position of secondary ion beam anomalously large
SA05/26 - 15a	15	0.0020149	0.0000002			5.8		0.054		c1	rejected, crack

**Appendix 2e**  
**Zircon oxygen isotope data of the Etive pluton and average values of bracketing zircon standard 91500**

analyses no.	grain no.	$^{18}\text{O}/^{16}\text{O}$ (measured)	2SD	1 s.e.m.	$^{18}\text{O}/^{16}\text{O}$ (drift corrected)	$\delta^{18}\text{O}$ [‰] VSMOW	2SD	1 s.e.m.	n	grain area	comment
SA05/26 - 16a	16	0.0020176		0.0000003		7.2		0.102		c2	
SA05/26 - 16b	16	0.0020164		0.0000003		6.6		0.113		rim	
SA05/26 - 17a	17	0.0020156		0.0000003		6.2		0.079		rim	
SA05/26 - 17b	17	0.0020154		0.0000004		6.1		0.131		c2	rejected, crack
SA05/26 - 19a	19	0.0020166		0.0000002		6.7		0.067		c1	rejected, crack
SA05/26 - 19b	19	0.0020145		0.0000003		5.7		0.087		c2	rejected, crack
SA05/26 - 20a	20	0.0020114		0.0000002		4.1		0.046		c1b	rejected, correction on position of secondary ion beam anomalously large
Mount4/91500 - 46-47, 49-50		0.0020230	0.0000006	0.0000002		9.70	0.6	0.157	4		
SA05/26 - 20c	20	0.0020153		0.0000002		6.0		0.065		c1a	
SA05/26 - 20b	20	0.0020163		0.0000003		6.5		0.091		rim	
SA05/26 - 21a	21	0.0020157		0.0000002		6.2		0.074		c2a	
SA05/26 - 21b	21	0.0020162		0.0000003		6.5		0.104		c2b	
SA05/26 - 23a	23	0.0020155		0.0000003		6.1		0.102		c1	rejected, crack
SA05/26 - 25a	25	0.0020160		0.0000004		6.4		0.130		rim	
SA05/26 - 27a	27	0.0020163		0.0000002		6.5		0.069		c2	
SA05/26 - 27b	27	0.0020138		0.0000003		5.3		0.091		r1a	
SA05/26 - 27c	27	0.0020144		0.0000004		5.6		0.110		r1b	rejected, crack
<b>Q-23</b>											
SA05/23 - 22a	22	0.0020166		0.0000004		6.7		0.139		c1	
SA05/23 - 22b	22	0.0020144		0.0000003		5.6		0.082		c2b	rejected, crack
SA05/23 - 21a	21	0.0020157		0.0000004		6.2		0.115		c2	
SA05/23 - 20a	20	0.0020164		0.0000002		6.6		0.057		c2a	rejected, crack
SA05/23 - 20b	20	0.0020139		0.0000002		5.4		0.058		c2b	rejected, correction on position of secondary ion beam anomalously large rejected, crack
SA05/23 - 19a	19	0.0020160		0.0000004		6.4		0.119		c1	
Mount4/91500 - 56-60		0.0020231	0.0000005	0.0000001		9.88	0.2	0.051	5		
SA05/23 - 19b	19	0.0020110		0.0000003		3.9		0.060		c2	rejected, correction on position of secondary ion beam anomalously large
SA05/23 - 18a	18	0.0020157		0.0000003		6.2		0.105		c2	
SA05/23 - 17a	17	0.0020166		0.0000002		6.7		0.076		c1a	rejected, correction on position of secondary ion beam anomalously large rejected, grain altered
SA05/23 - 17b	17	0.0020149		0.0000004		5.8		0.107		c1b	
SA05/23 - 16a	16	0.0020177		0.0000002		7.2		0.074		c2a	
SA05/23 - 16b	16	0.0020166		0.0000005		6.7		0.167		c2b	
SA05/23 - 15a	15	0.0020150		0.0000003		5.9		0.078		c1	
SA05/23 - 14a	14	0.0020132		0.0000004		5.0		0.089		c1b	rejected, crack
SA05/23 - 13a	13	0.0020170		0.0000002		6.9		0.082		c1	rejected, inclusion
SA05/23 - 14c	14	0.0020144		0.0000003		5.6		0.091		c1a	rejected, crack
Mount4/91500 - 61-65		0.0020231	0.0000010	0.0000002		9.87	0.5	0.106	5		
SA05/23 - 12a	12	0.0020137		0.0000004		5.3		0.096		c1b	rejected, correction on position of secondary ion beam anomalously large
SA05/23 - 12b	12	0.0020169		0.0000002		6.8		0.083		c1a	
SA05/23 - 11a	11	0.0020155		0.0000005		6.1		0.161		c2	
SA05/23 - 10a	10	0.0020149		0.0000003		5.8		0.088		c2b	
SA05/23 - 10b	10	0.0020162		0.0000004		6.5		0.126		c2a	
SA05/23 - 9a	9	0.0020152		0.0000002		6.0		0.059		c2	
SA05/23 - 8a	8	0.0020154		0.0000004		6.1		0.134		c2	
SA05/23 - 7a	7	0.0020166		0.0000001		6.7		0.048		c1	
SA05/23 - 6a	6	0.0020143		0.0000002		5.5		0.054		c2a	
SA05/23 - 5a	5	0.0020156		0.0000004		6.2		0.123		c2	
Mount4/91500 - 66-67, 69-70		0.0020228	0.0000003	0.0000001		9.55	0.7	0.170	4		
<b>Session 8 (13.06.2006)</b>											
Mount4/91500 - 81-84, 86-90		0.0020207	0.0000006	0.0000001		9.76	0.3	0.046	9		
SA05/23 - 6b	6	0.0020127		0.0000003		5.8		0.053		c2b	rejected, correction on position of secondary ion beam anomalously large rejected, crack
SA05/23 - 2a	2	0.0020134		0.0000003		6.2		0.090		c2	
SA05/23 - 1a	1	0.0020129		0.0000003		5.9		0.093		c1	
SA05/23 - 23a	23	0.0020138		0.0000003		6.4		0.070		c1	rejected, correction on position of secondary ion beam anomalously large
Mount4/91500 - 91-95		0.0020211	0.0000006	0.0000001		9.98	0.3	0.115	5		
<b>Q-25</b>											
SA05/25 - 1a	1	0.0020133		0.0000004		6.1		0.114		c2a	rejected, crack
SA05/25 - 1b	1	0.0020098		0.0000003		4.4		0.059		c2b	rejected, crack
SA05/25 - 2a	2	0.0020108		0.0000004		4.9		0.090		c2	rejected, crack
SA05/25 - 3a	3	0.0020103		0.0000002		4.6		0.056		c2	rejected, correction on position of secondary ion beam anomalously large
SA05/25 - 4a	4	0.0020129		0.0000005		5.9		0.150		c2	
SA05/25 - 6a	6	0.0020142		0.0000003		6.5		0.093		c2	
SA05/25 - 7a	7	0.0020111		0.0000002		5.0		0.052		c2	rejected, crack
SA05/25 - 8a	8	0.0020117		0.0000003		5.3		0.071		c2	rejected, crack
SA05/25 - 9a	9	0.0020123		0.0000002		5.6		0.044		c1	
SA05/25 - 10a	10	0.0020109		0.0000005		4.9		0.134		c2b	
Mount4/91500 - 96-100		0.0020209	0.0000010	0.0000002		9.90	0.5	0.107	5		
SA05/25 - 11a	11	0.0020147		0.0000004		6.8		0.125		c2	
SA05/25 - 12a	12	0.0020121		0.0000005		5.5		0.131		c2	rejected, crack
SA05/25 - 14a	14	0.0020134		0.0000003		6.2		0.084		c2	rejected, crack
SA05/25 - 15a	15	0.0020110		0.0000004		5.0		0.106			
SA05/25 - 16a	16	0.0020133		0.0000004		6.1		0.116		c2	

**Appendix 2e**  
**Zircon oxygen isotope data of the Etive pluton and average values of bracketing zircon standard 91500**

analyses no.	grain no.	$^{18}\text{O}/^{16}\text{O}$ (measured)	2SD	1 s.e.m.	$^{18}\text{O}/^{16}\text{O}$ (drift corrected)	$\delta^{18}\text{O}$ [‰] VSMOW	2SD	1 s.e.m.	n	grain area	comment
SA05/25 - 17a	17	0.0020110		0.0000005		5.0		0.135		c2	rejected, correction on position of secondary ion beam anomalously large
SA05/25 - 18b	18	0.0020129		0.0000003		5.9		0.097		c2	rejected, crack
SA05/25 - 19b	19	0.0020126		0.0000005		5.8		0.151		c2	rejected, crack
SA05/25 - 20c	20	0.0020130		0.0000004		5.9		0.116		c2	rejected, correction on position of secondary ion beam anomalously large
SA05/25 - 21a	21	0.0020113		0.0000003		5.1		0.086		c2a	rejected, crack
Mount4/91500 - 106-110		0.0020209	0.0000004	0.0000001		9.87	0.2	0.039	5		
SA05/25 - 21b	21	0.0020136		0.0000004		6.3		0.120		c2b	rejected, correction on position of secondary ion beam anomalously large
SA05/25 - 22a	22	0.0020138		0.0000004		6.4		0.122		c2	rejected, correction on position of secondary ion beam anomalously large
SA05/25 - 23a	23	0.0020120		0.0000004		5.5		0.096		c2	rejected, crack
SA05/25 - 24a	24	0.0020159		0.0000002		7.4		0.063		c2a	rejected, crack
SA05/25 - 24b	24	0.0020149		0.0000004		6.9		0.138		c2b	
SA05/25 - 25a	25	0.0020136		0.0000004		6.3		0.112		c2	
Session 9 (13.06.2006)											
Mount4/91500 - 111-115		0.0020203	0.0000008	0.0000002		9.82	0.4	0.088	5		
Mount3/91500 - 1-5, 7-9		0.0020204	0.0000013	0.0000002		9.84	0.7	0.117	8		
Cr-11	SA05/11 - 1a	1	0.0020136		0.0000002	6.5		0.060		c1	
	SA05/11 - 1b	1	0.0020120		0.0000004	5.7		0.113		rim	
	SA05/11 - 3a	3	0.0020136		0.0000003	6.5		0.092		c1	
	SA05/11 - 3b	3	0.0020123		0.0000002	5.8		0.059		rim	
	SA05/11 - 2a	2	0.0020134		0.0000004	6.4		0.117		c1	
	SA05/11 - 2b	2	0.0020106		0.0000004	5.0		0.109		c2	rejected, correction on position of secondary ion beam anomalously large
	SA05/11 - 6a	6	0.0020140		0.0000004	6.7		0.128		c2	rejected, correction on position of secondary ion beam anomalously large
	SA05/11 - 8a	8	0.0020161		0.0000003	7.7		0.133		c2a	
	SA05/11 - 8b	8	0.0020126		0.0000003	6.0		0.102		c2b	
	SA05/11 - 9b	9	0.0020147		0.0000003	7.0		0.093		rim	
	Mount3/91500 - 16-20		0.0020206	0.0000009	0.0000002	9.93	0.4	0.098	5		
	SA05/11 - 5a	5	0.0020143		0.0000003	6.8		0.100		c2	
	SA05/11 - 5b	5	0.0020146		0.0000006	7.0		0.202		rim	
	SA05/11 - 7a	7	0.0020148		0.0000004	7.1		0.137		c1	
	SA05/11 - 7b	7	0.0020136		0.0000003	6.5		0.102		c2	
	SA05/11 - 9a	9	0.0020157		0.0000003	7.5		0.121		c1	
	SA05/11 - 10a	10	0.0020155		0.0000002	7.4		0.066		c2a	rejected, scratch
	SA05/11 - 10b	10	0.0020139		0.0000005	6.6		0.165		c2b	
	SA05/11 - 11a	11	0.0020087		0.0000003	4.1		0.069		c1b	rejected, correction on position of secondary ion beam anomalously large
	SA05/11 - 11b	11	0.0020933		0.0000323	45.9		70.902		r1a	rejected, crack
	SA05/11 - 14a	14	0.0020155		0.0000003	7.4		0.107		c2a	rejected, correction on position of secondary ion beam anomalously large
	Mount3/91500 - 23-25		0.0020205	0.0000003	0.0000001	9.89	0.1	0.033	3		
	SA05/11 - 14c	14	0.0020105		0.0000002	4.9		0.044		c2b	rejected, correction on position of secondary ion beam anomalously large
	SA05/11 - 11c	11	0.0020097		0.0000003	4.6		0.067		c1a	rejected, crack
	SA05/11 - 11d	11	0.0020360		0.0000009	17.6		0.761		r1b	rejected, crack
	SA05/11 - 17a	17	0.0020142		0.0000003	6.8		0.096		c2a	rejected, crack
	SA05/11 - 17b	17	0.0020153		0.0000004	7.3		0.136		c2b	
	SA05/11 - 20a	20	0.0020164		0.0000004	7.9		0.173		c2a	
	SA05/11 - 20b	20	0.0020161		0.0000002	7.7		0.079		c2b	
	SA05/11 - 20c	20	0.0020158		0.0000003	7.6		0.113		c2c	
	SA05/11 - 20d	20	0.0020163		0.0000004	7.8		0.142		c2d	
	SA05/11 - 23a	23	0.0020147		0.0000002	7.0		0.054		c2	
	Mount3/91500 - 26-30		0.0020205	0.0000008	0.0000002	9.89	0.4	0.093	5		
	SA05/11 - 21a	21	0.0020095		0.0000005	4.5		0.100		c2a	rejected, correction on position of secondary ion beam anomalously large
	SA05/11 - 21c	21	0.0020141		0.0000004	6.8		0.144		c2c	rejected, correction on position of secondary ion beam anomalously large
	SA05/11 - 21b	21	0.0020080		0.0000003	3.7		0.050		c2d	rejected, correction on position of secondary ion beam anomalously large
	SA05/11 - 21d	21	0.0020074		0.0000003	3.4		0.051		c2b	rejected, crack
	SA05/11 - 24a	24	0.0020050		0.0000003	2.2		0.036		c2a	rejected, crack
	SA05/11 - 17c	17	0.0020160		0.0000003	7.7		0.108		c2c	rejected, correction on position of secondary ion beam anomalously large
Cr-17	SA05/17 - 3a	3	0.0020100		0.0000006	4.7		0.131		c2c	rejected, correction on position of secondary ion beam anomalously large

**Appendix 2e**  
**Zircon oxygen isotope data of the Etive pluton and average values of bracketing zircon standard 91500**

analyses no.	grain no.	$^{18}\text{O}/^{16}\text{O}$ (measured)	2SD	1 s.e.m.	$^{18}\text{O}/^{16}\text{O}$ (drift corrected)	$\delta^{18}\text{O}$ [‰] VSMOW	2SD	1 s.e.m.	n	grain area	comment
SA05/17 - 3b	3	0.0020104		0.0000004		4.9		0.100		c2a	
SA05/17 - 4a	4	0.0020106		0.0000005		5.0		0.129		c1a	
SA05/17 - 4b	4	0.0020122		0.0000004		5.8		0.109		c1b	
Mount3/91500 - 31-33, 35		0.0020203	0.0000002	0.0000001		9.81	0.1	0.031	4		
SA05/17 - 5a	5	0.0020113		0.0000002		5.4		0.062		c2a	rejected, crack
SA05/17 - 5b	5	0.0020123		0.0000005		5.8		0.151		c2b	
SA05/17 - 6a	6	0.0020129		0.0000004		6.2		0.120		inh	inherited
SA05/17 - 6b	6	0.0020100		0.0000004		4.7		0.085		r1a	
SA05/17 - 7a	7	0.0020118		0.0000004		5.6		0.110		c2a	rejected, > 20 % discordant
SA05/17 - 7b	7	0.0020144		0.0000006		6.9		0.217		c2b	
SA05/17 - 7c	7	0.0020121		0.0000006		5.8		0.159		rim	
SA05/17 - 8a	8	0.0020097		0.0000005		4.6		0.103		c2a	
SA05/17 - 8c	8	0.0020097		0.0000005		4.6		0.111		c2c	
SA05/17 - 10a	10	0.0020120		0.0000004		5.7		0.114		c1b	
Session 10 (14.06.2006)											
Mount2/91500 - 1-4, 6-9		0.0020210	0.0000010	0.0000002	0.0020214	9.64	0.4	0.075	9		
Mount2/91500 - 11-20		0.0020221	0.0000011	0.0000002	0.0020216	10.12	0.5	0.084	10		
SI-06	SA05/06 - 1a	1	0.0020146		0.0000002	6.4		0.065		c1	
	SA05/06 - 1b	1	0.0020150		0.0000002	6.6		0.077		rim	
	SA05/06 - 2a	2	0.0020132		0.0000003	5.6		0.073		c1	rejected, crack
	SA05/06 - 3a	3	0.0020156		0.0000002	6.8		0.076		c1	rejected, correction on position of secondary ion beam anomalously large
	SA05/06 - 4a	4	0.0020153		0.0000003	6.7		0.094		c1	rejected, crack
	SA05/06 - 5a	5	0.0020149		0.0000003	6.5		0.082		c1	rejected, crack
	SA05/06 - 5b	5	0.0020158		0.0000002	6.9		0.079		c2	rejected, crack
	SA05/06 - 6a	6	0.0020161		0.0000002	7.0		0.068		c2	
	SA05/06 - 7a	7	0.0020158		0.0000003	6.9		0.108		rim	
	SA05/06 - 8a	8	0.0020145		0.0000003	6.2		0.088		c2a	rejected, crack
	Mount2/91500 - 21-25		0.0020218	0.0000010	0.0000002	0.0020219	9.82	0.5	0.108	5	
	SA05/06 - 8b	8	0.0020138		0.0000003	5.8		0.073		c2b	rejected, correction on position of secondary ion beam anomalously large
	SA05/06 - 9a	9	0.0020158		0.0000001	6.8		0.048		c1	
	SA05/06 - 10a	10	0.0020146		0.0000003	6.2		0.080		c2	rejected, crack
	SA05/06 - 11a	11	0.0020151		0.0000003	6.5		0.082		c1	
	SA05/06 - 11c	11	0.0020131		0.0000003	5.4		0.086		c2	rejected, crack
	SA05/06 - 12a	12	0.0020136		0.0000003	5.7		0.075		c2	rejected, crack
	SA05/06 - 13b	13	0.0020101		0.0000003	3.9		0.063		c2	rejected, correction on position of secondary ion beam anomalously large
	SA05/06 - 14a	14	0.0020158		0.0000003	6.8		0.112		c2a	rejected, correction on position of secondary ion beam anomalously large
	SA05/06 - 14b	14	0.0020143		0.0000003	6.0		0.081		c2b	
	SA05/06 - 15a	15	0.0020146		0.0000003	6.1		0.099		c2a	
	Mount2/91500 - 26-30		0.0020224	0.0000008	0.0000002	0.0020222	9.96	0.4	0.089	5	
	SA05/06 - 15b	15	0.0020147		0.0000003	6.1		0.103		c2b	
	SA05/06 - 16a	16	0.0020151		0.0000002	6.3		0.071		r1a	
	SA05/06 - 16b	16	0.0020152		0.0000003	6.3		0.106		r1b	rejected, crack
	SA05/06 - 17a	17	0.0020144		0.0000003	5.9		0.078		c1	
	SA05/06 - 18a	18	0.0020139		0.0000003	5.7		0.082		r1a	rejected, correction on position of secondary ion beam anomalously large
	SA05/06 - 18b	18	0.0020138		0.0000002	5.6		0.056		r1b	
	SA05/06 - 18c	18	0.0020156		0.0000002	6.5		0.080		r2	
	SA05/06 - 19a	19	0.0020130		0.0000002	5.2		0.049		c2	rejected, correction on position of secondary ion beam anomalously large
	SA05/06 - 19b	19	0.0020155		0.0000002	6.5		0.060		rim	rejected, correction on position of secondary ion beam anomalously large
	SA05/06 - 20a	20	0.0020116		0.0000003	4.5		0.060		c1	rejected, crack
	Mount2/91500 - 31-34		0.0020223	0.0000011	0.0000003	0.0020225	9.78	0.5	0.137	4	
	SA05/06 - 20b	20	0.0020110		0.0000001	4.1		0.026		rim	rejected, crack
	SA05/06 - 21a	21	0.0020131		0.0000001	5.2		0.036		c1	rejected, crack
	SA05/06 - 21b	21	0.0020132		0.0000001	5.2		0.033		rim	rejected, crack
	Mount2/91500 - 36-40		0.0020227	0.0000008	0.0000002	0.0020226	9.89	0.4	0.085	5	
	Mount3/91500 - 41-50		0.0020227	0.0000009	0.0000001	0.0020228	9.78	0.5	0.074	10	
Cr-17	SA05/17 - 10b	10	0.0020165		0.0000002	6.7		0.062		c1c	
	SA05/17 - 12a	12	0.0020170		0.0000001	6.9		0.033		r1a	
	SA05/17 - 12b	12	0.0020173		0.0000003	7.0		0.094		r1b	rejected, crack
	SA05/17 - 10c	10	0.0020153		0.0000002	6.1		0.063		c1a	
	SA05/17 - 13a	13	0.0020165		0.0000002	6.6		0.061		c2	
	SA05/17 - 14a	14	0.0020162		0.0000002	6.5		0.069		c1a	
	SA05/17 - 14b	14	0.0020185		0.0000002	7.6		0.070		c2a	
	SA05/17 - 17a	17	0.0020169		0.0000002	6.8		0.057		c1	
	SA05/17 - 17b	17	0.0020178		0.0000002	7.2		0.055		c2	
	SA05/17 - 19a	19	0.0020151		0.0000002	5.9		0.064		r1a	
	Mount3/91500 - 51-55		0.0020235	0.0000008	0.0000002	0.0020232	10.02	0.4	0.086	5	
	SA05/17 - 19c	19	0.0020151		0.0000003	5.9		0.075		r1b	rejected, correction on position of secondary ion beam anomalously large
	SA05/17 - 20a	20	0.0020185		0.0000003	7.5		0.107		c1	
	SA05/17 - 24a	24	0.0020160		0.0000003	6.2		0.096		c2	

Appendix 2e

Zircon oxygen isotope data of the Etive pluton and average values of bracketing zircon standard 91500

analyses no.	grain no.	$^{18}\text{O}/^{16}\text{O}$ (measured)	2SD	1 s.e.m.	$^{18}\text{O}/^{16}\text{O}$ (drift corrected)	$\delta^{18}\text{O}$ [‰] VSMOW	2SD	1 s.e.m.	n	grain area	comment
SA05/17 - 24b	24	0.0020156		0.0000001		6.1		0.030		rim	
SA05/17 - 3c	3	0.0020157		0.0000004		6.1		0.107		c2b	rejected, crack
SA05/17 - 4c	4	0.0020154		0.0000002		5.9		0.069		c1c	
SA05/17 - 6c	6	0.0020186		0.0000002		7.5		0.073		r1a	
Session 11 (19.06.2006)											
91500/12 - 11-20		0.0020166	0.0000008	0.0000001		9.86	0.4	0.064	10		
91500/12 - 31-40		0.0020166	0.0000009	0.0000001		9.83	0.4	0.071	10		
Mount1/91500 - 1-9		0.0020168	0.0000015	0.0000002		9.93	0.7	0.120	9		
<b>MO</b>											
SA05/20 - 2b	2	0.0020083		0.0000003		5.7		0.077		c2	
SA05/20 - 3a	3	0.0020107		0.0000003		6.9		0.100		c2	
SA05/20 - 3b	3	-0.0012666		0.0000152		-1618.2				rim	analytical problem
SA05/20 - 4a	4	-0.0010095		0.0000129		-1490.7				c2a	analytical problem
SA05/20 - 4c	4	0.0020123		0.0000005		7.1		0.174		c2b	rejected, correction on position of secondary ion beam anomalously large
SA05/20 - 5a	5	0.0020141		0.0000004		8.0		0.148		c2a	rejected, correction on position of secondary ion beam anomalously large
SA05/20 - 6a	6	0.0020115		0.0000004		6.6		0.141		c2	
SA05/20 - 6b	6	0.0020104		0.0000003		6.1		0.093		rim	
SA05/20 - 7a	7	0.0020137		0.0000003		7.7		0.117		c2	
SA05/20 - 8a	8	0.0020106		0.0000004		6.2		0.133		c2a	
SA05/20 - 8b	8	0.0020103		0.0000003		6.1		0.101		c2b	
SA05/20 - 9a	9	0.0020099		0.0000006		5.8		0.169		c1	
SA05/20 - 9b	9	0.0020091		0.0000004		5.5		0.110		c2	
SA05/20 - 10a	10	0.0020098		0.0000004		5.8		0.120		c1	rejected, crack
Mount1/91500 - 20-21, 23-25		0.0020166	0.0000006	0.0000001		9.83	0.3	0.064	5		
SA05/20 - 10b	10	0.0020093		0.0000003		6.2		0.103		c2b	
SA05/20 - 11a	11	0.0020093		0.0000005		6.2		0.165		c1	
SA05/20 - 11b	11	0.0020128		0.0000005		7.9		0.196		c2	rejected, crack
SA05/20 - 12a	12	0.0020096		0.0000004		6.3		0.140		r1a	rejected, correction on position of secondary ion beam anomalously large
SA05/20 - 12b	12	0.0020090		0.0000005		6.1		0.155		r1b	
SA05/20 - 13a	13	0.0020107		0.0000003		6.9		0.092		rim	
SA05/20 - 14a	14	0.0020133		0.0000003		8.2		0.107		c2b	
SA05/20 - 15a	15	0.0020106		0.0000005		6.9		0.171		c2a	

**Appendix 2e**  
**Zircon oxygen isotope data of the Etive pluton and average values of bracketing zircon standard 91500**

analyses no.	grain no.	$^{18}\text{O}/^{16}\text{O}$ (measured)	2SD	1 s.e.m.	$^{18}\text{O}/^{16}\text{O}$ (drift corrected)	$\delta^{18}\text{O}$ [‰] VSMOW	2SD	1 s.e.m.	n	grain area	comment
SA05/20 - 14b	14	0.0020089		0.0000003		6.0		0.092		c2a	rejected, correction on position of secondary ion beam anomalously large
SA05/20 - 15b	15	0.0020102		0.0000004		6.6		0.128		c2b	
Mount1/91500 - 26-30		0.0020166	0.0000019	0.0000004		9.83	0.9	0.206	5		
SA05/20 - 16a	16	0.0020100		0.0000005		6.6		0.159		r1a	rejected, correction on position of secondary ion beam anomalously large
SA05/20 - 16b	16	0.0020100		0.0000004		6.6		0.126		r1b	rejected, correction on position of secondary ion beam anomalously large
SA05/20 - 17a	17	0.0020090		0.0000006		6.1		0.189		c1	rejected, correction on position of secondary ion beam anomalously large
SA05/20 - 17b	17	0.0020084		0.0000004		5.8		0.106		c2	rejected, correction on position of secondary ion beam anomalously large
SA05/20 - 18a	18	0.0020069		0.0000004		5.0		0.092		c1	rejected, crack
SA05/20 - 18b	18	0.0020081		0.0000005		5.6		0.135		c2	
SA05/20 - 19a	19	0.0020099		0.0000004		6.5		0.143		c2a	
SA05/20 - 19b	19	0.0020085		0.0000004		5.8		0.112		rim	
<b>Session 12 (19.06.2006)</b>											
Mount1/91500 - 26-30		0.0020155	0.0000013	0.0000003		9.86	0.6	0.145	5		
<b>Session 13 (15.11.2006)</b>											
Mount1/91500 - 1-10		0.0020195	0.0000006	0.0000001	0.0020197	9.76	0.3	0.052	10		
Mount1/91500 - 11-20		0.0020195	0.0000004	0.0000001	0.0020195	9.86	0.2	0.035	10		
Mount1/91500 - 21-25, 27-30		0.0020195	0.0000007	0.0000001	0.0020190	10.11	0.4	0.060	9		
SA05/20 - 17a.2	17	0.0020124		0.0000013		6.8		0.451		c1	
SA05/20 - 17b.2	17	0.0020119		0.0000004		6.6		0.132		c2	
Mount1/91500 - 31-35		0.0020181	0.0000015	0.0000003	0.0020185	9.64	0.8	0.168	5		
Mount1/91500 - 36-39		0.0020185	0.0000006	0.0000002	0.0020184	9.88	0.3	0.073	4		
SA05/20 - 14b.2	14	0.0020128		0.0000002		7.1		0.078		c2a	
SA05/20 - 14a.2	14	0.0020122		0.0000002		6.8		0.068		c2b	
SA05/20 - 12a.2	12	0.0020138		0.0000007		7.6		0.267		r1a	rejected, crack
SA05/20 - 12b.2	12	0.0020122		0.0000011		6.9		0.367		r1b	
SA05/20 - 10c	10	0.0020116		0.0000005		6.6		0.166		c2a	
SA05/20 - 5a.2	5	0.0020114		0.0000012		6.5		0.386		c2a	
SA05/20 - 5c	5	0.0020122		0.0000009		6.9		0.293		c2b	
SA05/20 - 4c.2	4	0.0020130		0.0000011		7.3		0.403		c2b	
SA05/20 - 4a.2	4	0.0020113		0.0000006		6.5		0.208		c2a	
SA05/20 - 1c	1	0.0020107		0.0000006		6.2		0.170			
Mount1/91500 - 42-45		0.0020179	0.0000008	0.0000002	0.0020181	9.80	0.4	0.101	4		
<b>Session 14 (15.11.2006)</b>											
Mount3/91500 - 46-49		0.0020176	0.0000005	0.0000001		9.78	0.3	0.065	4		
91500 - 0-4		0.0020177	0.0000002	0.0000001		9.85	0.1	0.028	4		
<b>Cr-17</b>											
SA05/17 - 3d	3	0.0020077		0.0000014		4.9		0.352		c2d	rejected, crack
SA05/17 - 3b	3	0.0020110		0.0000004		6.5		0.114		c2a	
SA05/17 - 4d	4	0.0020117		0.0000003		6.9		0.089		c1b	
SA05/17 - 4e	4	0.0020096		0.0000003		5.8		0.095		c2b	rejected, crack
SA05/17 - 6c	6	0.0020115		0.0000003		6.8		0.115		r1a	
SA05/17 - 6d	6	0.0020109		0.0000002		6.5		0.057		r1c	
SA05/17 - 10a	10	0.0020114		0.0000007		6.7		0.242		c1b	
SA05/17 - 10c	10	0.0020123		0.0000029		7.2		1.026		c1a	
SA05/17 - 10b	10	0.0020105		0.0000032		6.3		0.997		c1c	
SA05/17 - 14d	14	0.0020116		0.0000003		6.8		0.087		c1b	rejected, crack
Mount3/91500 - 51-55		0.0020178	0.0000006	0.0000001		9.91	0.3	0.062	5		
SA05/17 - 14e	14	0.0020114		0.0000002		6.7		0.051		c2b	
SA05/17 - 14f	14	0.0020118		0.0000002		6.9		0.080		c2c	
<b>Cr-11</b>											
SA05/11 - 10a	10	0.0020120		0.0000004		7.0		0.145		c2a	
SA05/11 - 10b	10	0.0020108		0.0000003		6.4		0.108		c2b	
SA05/11 - 11a	11	0.0020122		0.0000002		7.1		0.088		c1b	
SA05/11 - 11b	11	0.0020110		0.0000006		6.5		0.205		r1a	
SA05/11 - 11e	11	0.0020120		0.0000004		7.0		0.151		c1c	
SA05/11 - 11d	11	0.0020128		0.0000013		7.4		0.483		r1b	
SA05/11 - 17a	17	0.0020123		0.0000016		7.2		0.587		c2a	rejected, crack
SA05/11 - 17b	17	0.0020135		0.0000002		7.7		0.095		c2b	rejected, crack
SA05/11 - 21a	21	0.0020102		0.0000003		6.2		0.089		c2a	rejected, correction on position of secondary ion beam anomalously large
SA05/11 - 21c	21	0.0020097		0.0000003		5.9		0.083		c2c	rejected, correction on position of secondary ion beam anomalously large
SA05/11 - 21d	21	0.0020104		0.0000005		6.2		0.141		c2b	rejected, correction on position of secondary ion beam anomalously large
SA05/11 - 24a	24	0.0020127		0.0000003		7.4		0.102		c2a	rejected, crack
SA05/11 - 24b	24	0.0020112		0.0000003		6.6		0.089		c2b	rejected, grain altered
Mount3/91500 - 56-60		0.0020178	0.0000005	0.0000001		9.88	0.2	0.051	5		











sample	analysis no.	grain U no.	Th ppm	Pb ppm	Th/U ppb	<sup>204</sup> Pb/ ppb	<sup>206</sup> Pb/ <sup>204</sup> Pb	corrected ratios				Ages (Ma)				grain comment area		
								<sup>207</sup> Pb/ <sup>206</sup> Pb	1σ	<sup>208</sup> Pb/ <sup>206</sup> Pb	1σ	<sup>207</sup> Pb/ 1σ	<sup>208</sup> Pb/ 1σ	<sup>206</sup> Pb/ <sup>235</sup> U	<sup>207</sup> Pb/ 1σ		% disc	
91500		80	28	15	0.36	0.3	0.04	0.0000224	0.0745	0.0007	0.1066	0.0010	1.8475	0.0235	1.799	0.0016	0.69	-1.2
91500		81	28	15	0.36	0.0	0.01	0.0000028	0.0742	0.0006	0.1075	0.0007	1.8109	0.0231	1.769	0.0017	0.73	-0.2
91500		82	29	15	0.36	0.0	0.00	0.0000001	0.0751	0.0007	0.1084	0.0008	1.8391	0.0247	1.776	0.0016	0.69	1.6
91500		83	29	15	0.36	0.0	0.00	0.0000001	0.0748	0.0006	0.1087	0.0009	1.8337	0.0221	1.779	0.0017	0.77	0.6
91500		83	29	15	0.36	0.0	0.00	0.0000001	0.0758	0.0009	0.1081	0.0012	1.8794	0.0291	1.798	0.0018	0.62	2.0
91500		82	29	15	0.36	0.5	0.07	0.0000397	0.0738	0.0006	0.1063	0.0014	1.8451	0.0229	1.814	0.0016	0.71	-3.8
91500		80	28	15	0.35	0.0	0.00	0.0000001	0.0752	0.0007	0.1070	0.0009	1.8648	0.0242	1.818	0.0017	0.71	-0.3
91500		80	28	15	0.36	0.1	0.02	0.0000120	0.0742	0.0007	0.1061	0.0012	1.8234	0.0240	1.782	0.0017	0.71	-1.1
91500		81	28	15	0.36	0.5	0.08	0.0000412	0.0742	0.0007	0.1061	0.0012	1.8234	0.0240	1.782	0.0017	0.71	-1.1
91500		82	29	15	0.36	0.0	0.00	0.0000001	0.0745	0.0005	0.1068	0.0008	1.8436	0.0219	1.801	0.0017	0.80	-2.0
91500		81	28	15	0.36	0.0	0.00	0.0000001	0.0747	0.0008	0.1073	0.0007	1.8485	0.0245	1.795	0.0015	0.65	-0.5
91500		79	27	14	0.35	0.0	0.00	0.0000001	0.0745	0.0005	0.1073	0.0010	1.8187	0.0201	1.770	0.0016	0.82	0.4
91500		80	28	15	0.35	0.0	0.01	0.0000027	0.0744	0.0007	0.1075	0.0004	1.8175	0.0232	1.772	0.0016	0.71	0.0
91500		81	28	15	0.35	0.4	0.06	0.0000326	0.0751	0.0007	0.1065	0.0012	1.8482	0.0242	1.786	0.0016	0.68	1.0
91500		84	29	15	0.36	0.3	0.04	0.0000224	0.0738	0.0010	0.1078	0.0012	1.8248	0.0287	1.793	0.0016	0.57	-2.6
91500		80	28	15	0.35	0.0	0.01	0.0000029	0.0751	0.0007	0.1067	0.0008	1.8675	0.0241	1.804	0.0017	0.73	0.1
91500		80	27	15	0.35	0.6	0.09	0.0000468	0.0746	0.0009	0.1065	0.0015	1.8341	0.0277	1.783	0.0016	0.60	-0.1
91500		81	29	15	0.36	0.0	0.00	0.0000001	0.0756	0.0009	0.1085	0.0011	1.8676	0.0378	1.792	0.0029	0.79	2.0
91500		83	29	15	0.36	0.5	0.08	0.0000405	0.0747	0.0007	0.1066	0.0014	1.8764	0.0268	1.821	0.0019	0.72	-1.6
91500		85	29	16	0.36	0.1	0.01	0.0000072	0.0754	0.0008	0.1069	0.0009	1.9060	0.0262	1.832	0.0017	0.67	-0.4
91500		80	28	15	0.35	0.4	0.05	0.0000283	0.0735	0.0007	0.1059	0.0013	1.8569	0.0256	1.832	0.0018	0.72	-5.6
91500		81	28	15	0.36	0.0	0.00	0.0000001	0.0748	0.0011	0.1053	0.0009	1.8544	0.0338	1.795	0.0018	0.58	0.2
91500		80	28	15	0.35	0.0	0.00	0.0000001	0.0743	0.0006	0.1081	0.0011	1.8304	0.0261	1.787	0.0020	0.79	-1.1
91500		83	29	15	0.36	0.5	0.07	0.0000362	0.0758	0.0008	0.1070	0.0016	1.8765	0.0282	1.795	0.0018	0.67	-1.1
91500		83	29	15	0.36	0.6	0.09	0.0000475	0.0733	0.0008	0.1070	0.0015	1.8039	0.0277	1.786	0.0018	0.67	-3.9
91500		84	29	16	0.36	0.0	0.00	0.0000001	0.0748	0.0006	0.1083	0.0010	1.8725	0.0248	1.816	0.0019	0.79	-1.3
91500		82	28	15	0.35	0.2	0.03	0.0000168	0.0759	0.0007	0.1070	0.0009	1.8797	0.0244	1.797	0.0017	0.71	2.3
91500		82	28	15	0.35	0.4	0.05	0.0000283	0.0743	0.0008	0.1068	0.0012	1.8441	0.0260	1.800	0.0017	0.69	-1.6
91500		80	28	15	0.36	0.4	0.06	0.0000300	0.0750	0.0009	0.1086	0.0013	1.8492	0.0284	1.789	0.0018	0.64	0.6
91500		80	28	14	0.36	0.0	0.00	0.0000001	0.0747	0.0008	0.1071	0.0010	1.8105	0.0269	1.759	0.0017	0.65	1.4
91500		76	26	14	0.35	0.4	0.06	0.0000319	0.0754	0.0007	0.1070	0.0012	1.8625	0.0254	1.793	0.0017	0.69	1.3
91500		80	28	15	0.36	0.6	0.09	0.0000463	0.0736	0.0009	0.1052	0.0015	1.8226	0.0300	1.795	0.0019	0.64	-3.3
91500		78	27	14	0.35	0.0	0.00	0.0000001	0.0746	0.0010	0.1083	0.0011	1.7915	0.0302	1.742	0.0019	0.65	2.1
91500		81	28	15	0.36	0.0	0.00	0.0000001	0.0741	0.0009	0.1073	0.0010	1.8001	0.0290	1.763	0.0018	0.62	-0.5
91500		82	29	15	0.36	0.0	0.00	0.0000001	0.0740	0.0009	0.1081	0.0009	1.7955	0.0283	1.759	0.0017	0.62	-0.2
91500		82	29	15	0.36	0.3	0.04	0.0000207	0.0747	0.0007	0.1082	0.0012	1.8439	0.0259	1.789	0.0019	0.74	0.0
91500		79	28	14	0.36	0.2	0.03	0.0000147	0.0749	0.0006	0.1097	0.0009	1.8427	0.0259	1.783	0.0020	0.80	0.8
91500		81	28	15	0.36	0.7	0.10	0.0000536	0.0766	0.0008	0.1061	0.0016	1.8813	0.0284	1.782	0.0020	0.73	4.7
91500		81	28	15	0.36	0.0	0.00	0.0000001	0.0744	0.0008	0.1087	0.0010	1.8234	0.0283	1.784	0.0019	0.70	-1.4
91500		83	29	15	0.36	0.0	0.00	0.0000001	0.0757	0.0007	0.1084	0.0011	1.8966	0.0288	1.817	0.0021	0.76	1.0
Session	temora	106	53	7	0.51	0.3	0.11	0.0000573	0.0542	0.0007	0.1625	0.0019	0.4785	0.0076	0.0640	0.0006	0.57	-5.9
		114	57	8	0.51	0.1	0.02	0.0000132	0.0554	0.0007	0.1593	0.0012	0.5185	0.0089	0.0678	0.0008	0.67	1.6





Cr-26													Q-23													
SA05/15		SA05/15		SA05/15		SA05/15		SA05/15		SA05/15		SA05/26		SA05/26		SA05/26		SA05/26		SA05/26		SA05/23		SA05/23		
4a	8a	9a	11a	11b	19a	19b	22a	22b	22c	26a	5a	6a	6b	12a	12b	16a	16b	20c	20b	27a	27b	5a	8a	9a	10a	
grain no.		4	8	9	11	11	19	19	22	22	26	5	6	6	12	16	16	20	20	27	27	5	8	9	10	
Si	140230	140230	140230	140230	140230	140230	140230	140230	140230	140230	140230	140230	140230	140230	140230	140230	140230	140230	140230	140230	140230	140230	140230	140230		
P	470	307	161	298	349	205	252	246	331	392	382	812	406	284	285	281	262	273	131	162	473	538	769	439	337	
Ca	21	20	9	16	5	6	87	5	6	7	2	17	13	6	14	13	3	5	5	5	28	5	6	12	13	
Ti	3529	21.89	6.28	16.54	8.64	36.90	9.60	10.44	11.99	4.76	11.95	4.76	12	11.14	8.74	15.68	12.00	7.42	10.95	7.73	7.42	7.85	11	17.69	22.03	
Y	827	658	657	911	519	1090	723	1234	886	1195	886	3909	1184	651	566	819	843	1147	266	394	2190	2948	4027	1933	744	
Nb	2	3	2	2	1	1	1	1	2	2	6	42	3	2	2	3	1	1	1	1	21	21	21	21	21	
Ba	569660	570070	565580	567410	543560	533740	539940	535940	526830	526090	526090	556790	549980	531160	544370	576150	558510	559140	556240	570300	532030	542230	533380	536270	548350	
La	0.0	0.2	0.1	0.0	0.1	0.0	0.0	0.0	0.1	0.1	0.1	0	0.2	0.1	0.1	0.1	0.1	0.0	0.1	-0.1	0.7	0	0.1	0.2	0.1	
Pr	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.5	0	0.5	0.2	0.0	
Sm	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.5	0	0.5	0.2	0.0	
Eu	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.5	0	0.5	0.2	0.0	
Gd	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.5	0	0.5	0.2	0.0	
Tb	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.5	0	0.5	0.2	0.0	
Dy	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.5	0	0.5	0.2	0.0	
Er	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.5	0	0.5	0.2	0.0	
Tm	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.5	0	0.5	0.2	0.0	
Yb	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.5	0	0.5	0.2	0.0	
Lu	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.5	0	0.5	0.2	0.0	
Hf	12318	12413	12606	9711	10225	9685	9505	8989	9005	9005	14103	2680	386	123	69	129	136	122	30	88	1550	1263	1261	355	189	
Th	14	71	81	92	44	128	66	130	82	286	286	2533	300	131	82	157	178	116	48	155	1718	786	889	319	269	
La	0.17	0.18	0.15	0.20	0.10	0.48	0.20	0.26	0.26	0.22	0.26	0.60	0.33	0.20	0.13	0.17	0.20	0.81	0.10	0.06	36.19	0.49	2.22	0.68	0.10	
Pr	35.8	59.2	69.6	64.8	41.6	68.3	52.5	60.9	61.6	132.9	132.9	466.8	148.6	86.2	50.9	87.7	94.2	65.1	41.8	42.4	302.6	149.3	150.9	65	14.2	
Nd	6.40	3.83	4.28	7.05	2.84	18.69	6.65	18.20	5.84	4.89	4.89	3.06	3.00	1.60	1.92	2.17	1.15	5.44	0.80	17.76	17.76	29.02	40.46	26.01	5.98	
Sm	36	20	24	33	12	62	29	58	30	27	27	90	45	25	20	30	21	64	8	14	59	112	162	92	11	
Eu	23	10	19	29	16	59	26	54	24	23	23	29	39	22	20	31	19	57	6	13	21	32	58	37	21	
Gd	124	76	84	103	55	192	93	191	92	71	71	693	263	154	125	196	168	326	62	45	249	426	681	333	99	
Tb	220	152	154	190	114	317	175	321	182	237	237	1836	519	268	235	347	297	532	105	150	906	1274	1921	883	32	
Dy	388	276	285	368	215	543	312	576	339	480	480	1936	519	268	235	347	297	532	105	150	906	1274	1921	883	32	
Er	914	777	785	1154	600	1243	832	1372	1040	1491	1491	4659	1399	730	637	979	812	1351	317	459	2502	3200	4536	2083	524	
Tm	1240	1162	1072	1692	868	1682	1187	1856	1540	2272	2272	6461	1967	1018	944	1400	1149	1690	479	694	3529	4536	2083	524	524	
Yb	1465	1465	1347	2163	1075	1922	1439	2118	1897	3045	3045	7763	2428	1201	1194	1818	1495	1614	991	1620	6366	4758	6230	3086	1475	
Lu	2197	2358	2156	3592	1842	3066	2443	3447	3220	4983	4983	11400	3801	2026	1988	2377	2284	3059	1017	1620	6366	6929	8940	4574	2300	
Hf	1194423	1193558	1212115	933731	963173	931221	913904	865827	864327	1356058	1356058	1377308	974423	975000	869692	1019808	1140000	977692	103654	1137019	1304615	1243173	1027404	971635	1151635	
Th	6	29	33	37	18	52	27	53	33	116	116	1085	156	50	28	52	55	49	12	35	628	373	511	144	80	
U	3683	10558	13610	15543	7720	12881	9594	14049	13522	58373	58373	382136	36877	16125	10130	19362	21958	14269	5892	19179	212049	97007	109743	35328	33160	
Th/U	0.47	0.83	0.73	0.70	1.22	0.85	1.15	0.74	0.61	0.61	0.61	0.91	1.29	0.94	0.84	0.83	0.76	1.05	0.64	0.56	0.90	1.17	1.42	1.11	0.74	
Yb/(La+Pr)	8713	7937	9116	11080	11203	4031	7089	8252	7209	13906	13906	13033	7464	6025	9183	7458	2403	6314	16949	119	16949	9730	2809	4532	14721	
Pr/Ce	11.8	9.4	16.0	20.9	19.5	10.0	15.5	11.1	20.6	42.7	42.7	19.2	16.5	14.6	16.0	15.5	17.0	8.6	21.8	22.0	17.2	91.0	9.1	9.3	14.9	
Pr/Ce*	11.8	9.4	16.0	20.9	19.5	10.0	15.5	11.1	20.6	42.7	42.7	19.2	16.5	14.6	16.0	15.5	17.0	8.6	21.8	22.0	17.2	91.0	9.1	9.3	14.9	
Ca/Ce*	84.9	135.0	154.5	98.0	138.3	40.4	74.7	49.8	89.9	24.3	24.3	345.6	150.4	152.7	102.0	143.8	196.0	31.0	218.7	195.1	11.9	69.5	24.9	20.8	190.5	
HfO <sub>2</sub> [wt%]	1.5	1.5	1.5	1.1	1.2	1.1	1.1	1.1	1.1	1.1	1.7	1.7	1.2	1.2	1.1	1.3	1.4	1.2	1.3	1.4	1.6	1.5	1.3	1.2	1.4	
comment	inherited	inherited	inherited	inherited	inherited	inherited	inherited	inherited	inherited	inherited	inherited	inherited	inherited	inherited	inherited	inherited	inherited	inherited	inherited	inherited	inherited	inherited	inherited	inherited	inherited	
grain area	rim	rim	rim	rim	rim	rim	rim	rim	rim	rim	rim	rim	rim	rim	rim	rim	rim	rim	rim	rim	rim	rim	rim	rim	rim	rim
	c2	c2	c2a	c2b	c1	c2	c1	c2	c1	c2	c1	c1	c1	c1	c2	c2b	c2	c2	c1a	rim	c2	c2	c2	c2	c2b	

grain no.	Gr-11										comment
	SA05/23 10b	SA05/23 7a	SA05/23 12b	SA05/23 14a	SA05/23 14c	SA05/23 16a	SA05/23 22a	SA05/23 22b	SA05/23 22c	SA05/23 22d	
10	7	12	14	14	16	16	22	22			
140230	140230	140230	140230	140230	140230	140230	140230	140230			
617	312	920	332	346	391	345	268	143			
7	178	19	5	21	24	18	14	43			
Ca	19.17	21.73	11.34	20.58	20.32	16	14.21	27.96	14.3		
Ti	2203	515	5009	615	535	1637	1849	514	364		
Nb	540770	547180	536030	540360	549310	549660	566080	543710	1		
Al	0.2	0.1	0.2	0.2	0.1	0.1	0.1	0.3			
Fe	504770	504770	504770	504770	504770	504770	504770	504770			
Cr	67.1	18.7	193.8	26.6	22.5	63	59.3	22	23		
Co	0.9	0.2	2.9	0.1	0.2	0.8	0	1			
Si	12.6	3.8	30.5	2.5	2.5	20	11.5	2	4		
Mn	15.6	3.2	31.8	4.3	3.5	15	14.7	3	2		
Ge	2.4	0.6	4.1	0.7	0.6	2	1.7	1			
U	80	15	161	19	16	59	66	15	8		
Y	255	53	568	69	54	200	223	55	33		
Ho	88	19	198	24	20	70	76	19	13		
Er	388	86	877	114	93	311	342	90	66		
Tm	78	19	177	24	19	61	67	19	16		
Yb	588	152	1334	200	159	492	522	157	147		
Lu	133	35	282	46	37	108	114	36	38		
La	10732	1523	12883	10543	11619	11895	11510	13425			
Pr	593	14	218	83	47	136	141	66	819		
Sm	596	91	1598	131	92	423	79	819			
La	0.63	0.67	12.81	0.12	0.17	6.57	0.36	0.11	6.27		
Pr	111.3	31.0	321.3	44.0	37.3	103.9	98.4	35.9	38.4		
Co	9.67	2.49	32.51	1.35	1.61	25.88	8.93	1.08	8.35		
Fe	27.79	6.19	67.29	5.47	5.45	44.94	25.52	4.24	8.85		
Nb	106	22	216	29	24	100	100	18	15		
Sm	468	76	818	97	80	302	335	74	41		
Er	646	126	1395	162	138	490	545	133	72		
Ho	1053	220	2332	283	224	823	919	227	134		
Yb	1588	337	3518	437	367	1257	1369	350	232		
Lu	2445	542	5520	718	597	1956	2151	567	414		
Er	3235	775	7505	982	750	2527	2776	785	647		
Nb	3620	933	5209	1228	960	3029	3211	968	964		
Al	5463	149	17637	1513	15327	14899	14689	15301	13501		
Fe	19123	1107801	1220481	1072212	1117212	143750	107331	106730	10665		
Co	235	22	962	33	35	192	174	27	21		
Th	6152	11220	197335	16226	11301	52695	52236	9731	101120		
La	0.55	0.60	1.33	0.63	0.71	1.11	1.02	0.58	0.98		
ThU	1292	641	10202	5692	461	8895	8825	144	144		
Yb(Nb/Lan)	5725	1396	60	120	10.0	9.6	13.1	21.9			
Yb(NbGdIn)	9.12	0.2	0.2	0.2	0.2	0.2	0.2	0.2			
Yb(NbErU)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2			
CoCeCo	45.0	24.0	15.7	109.2	70.9	80.0	54.8	104.2	5.3		
CH <sub>2</sub> CO <sub>2</sub>	1.3	1.4	1.5	1.3	1.2	1.4	1.4	1.6	1.6		
SA05/11 1a	SA05/11 1b	SA05/11 5a	SA05/11 5b	SA05/11 8a	SA05/11 8b	SA05/11 9a	SA05/11 9b	SA05/11 11c	SA05/11 20a	SA05/11 20d	
1	1	5	5	8	8	9	9	11	20	20	
140230	140230	140230	140230	140230	140230	140230	140230	140230	140230	140230	
208	203	311	253	252	345	345	170	362	480	282	
12	3	4	9	9	3	3	3	3	4	9	
6	8	11	7.91	9.11	9.63	11.62	5.16	11.20	12.20	8.99	
1067	1243	1467	783	1324	1383	1146	1050	2173	2839	931	
4	1	4	2	2	2	3	3	2	4	3	
550770	554830	554830	552380	539850	541380	546280	540680	544960	546980	542900	
0	0	0	0.1	0.1	0.1	0.1	0.0	0.1	0.2	0.1	
0	0	0	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.1	
37	38	61	35.2	40.3	46.6	40.4	45.2	85.0	41.7		
0	0	0	0.1	0.6	0.7	0.3	0.3	1.0	1.2	0.1	
6	8	5	2.2	9.4	10.5	3.5	5.7	13.8	17.1	2.5	
8	9	7	3.4	11.5	12.4	5.0	7.6	17.0	23.7	3.8	
3	3	10	3.8	4.1	1.6	2.4	6.1	8.1	1.1	1.1	
33	39	34	17	48	52	26	35	94	110	19	
117	133	142	71	152	165	112	113	256	337	82	
43	48	55	29	53	56	44	41	88	115	34	
197	223	273	150	236	248	215	194	395	504	176	
42	46	60	34	49	52	47	41	79	103	40	
81	92	121	77	92	97	100	60	146	186	90	
10723	10383	10689	10588	9531	9360	12694	9365	9546	10027		
137	141	150	106	132	137	188	132	185	202		
187	210	291	188	182	184	215	188	307	412	204	
0.19	0.37	0.36	0.18	0.28	0.48	0.22	0.20	0.56	0.79	0.19	
61.8	62.7	100.3	58.3	66.8	65.2	80.6	67.0	98.1	140.9	69.1	
6.66	6.36	12.9	7.04	7.41	7.41	3.25	11.09	13.05	13.05	1.35	
14.15	11.92	4.76	20.83	23.21	7.82	14.24	30.43	37.80	54.9		
55	53	48	23	78	95	34	51	116	161	26	
170	197	174	85	247	265	134	177	426	559	95	
280	316	321	155	393	415	271	276	650	868	176	
481	547	597	292	628	679	460	466	1056	1367	338	
770	857	988	513	953	1014	730	730	1535	2076	604	
1405	1741	1945	1483	1562	1533	1223	2483	3173	1105	1105	
1920	2484	2404	2005	2133	1958	1701	3273	4244	1671		
2111	2324	3680	1827	2440	2531	2081	3868	4967	2126		
1772	1970	3163	3503	3975	3503	3503	3503	3503	3503		
1262631	11058	95927	106558	101677	90008	90008	90008	90008	90008		
73	86	98	49	80	81	72	75	155	230	49	
23697	25967	35930	23235	23678	22667	26600	23152	37912	50974	25142	
0.96	1.00	0.84	0.64	1.04	1.09	0.83	0.99	1.25	1.07		
11210	6287	8598	10297	8699	5289	1188	10450	6939	6358	11012	
12.12	11.8	17.6	21.6	9.5	18.3	11.1	8.9	22.4	8.9		
0.5	0.5	0.4	0.5	0.5	0.5	0.5	0.5	0.5	0.5		
66.3	39.9	85.9	121.7	47.5	34.7	118.4	83.3	39.5	44.0	135.6	
1.4	1.3	1.2	1.2	1.2	1.1	1.1	1.4	1.1	1.1	1.2	
c1	rm	c2	rm	c2a	c2b	c1	rm	c1a	c2a	c2d	

MO	SA05/20		SA05/20		SA05/20		SA05/20		SA05/20		SA05/20		SA05/20		SA05/20		SA05/20	
	2a	2b	6a	7a	9a	9b	14a	18a	18b	18c	18d	18e	18f	18g	18h	18i		
grain no.	2	2	6	7	9	9	9	14	18	18	18	19	19	19	19	19		
Si	140/230	140/230	140/230	140/230	140/230	140/230	140/230	140/230	140/230	140/230	140/230	140/230	140/230	140/230	140/230	140/230		
Si	285	304	435	384	4036	390	291	595	333	324	534	297	297	297	297	297		
Ca	44	5	17	17	7	7	4	4	5	4	5	4	5	4	5	4		
Ti	11.28	9.04	17.11	106.94	12.89	10.91	13.02	10.93	10.51	10.51	11.59	11.12	11.12	11.12	11.12	11.12		
Al	1196	851	1505	1365	1333	760	1871	1096	811	742	1143	1143	1143	1143	1143	1143		
Nb	3	3	4	4	4	4	7	2	2	2	3	3	3	3	3	3		
505690	542900	575370	576990	565540	537440	546260	545240	549220	548450	539730	539730	539730	539730	539730	539730	539730		
0.2	0.1	0.1	17.6	0.1	0.2	0.1	0.2	0.0	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2		
0.3	0.1	0.1	17.6	0.1	0.2	0.1	0.2	0.0	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2		
0.4	0.1	0.1	17.6	0.1	0.2	0.1	0.2	0.0	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2		
0.5	0.1	0.1	17.6	0.1	0.2	0.1	0.2	0.0	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2		
0.6	0.1	0.1	17.6	0.1	0.2	0.1	0.2	0.0	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2		
0.7	0.1	0.1	17.6	0.1	0.2	0.1	0.2	0.0	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2		
0.8	0.1	0.1	17.6	0.1	0.2	0.1	0.2	0.0	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2		
0.9	0.1	0.1	17.6	0.1	0.2	0.1	0.2	0.0	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2		
1.0	0.1	0.1	17.6	0.1	0.2	0.1	0.2	0.0	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2		
1.1	0.1	0.1	17.6	0.1	0.2	0.1	0.2	0.0	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2		
1.2	0.1	0.1	17.6	0.1	0.2	0.1	0.2	0.0	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2		
1.3	0.1	0.1	17.6	0.1	0.2	0.1	0.2	0.0	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2		
1.4	0.1	0.1	17.6	0.1	0.2	0.1	0.2	0.0	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2		
1.5	0.1	0.1	17.6	0.1	0.2	0.1	0.2	0.0	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2		
1.6	0.1	0.1	17.6	0.1	0.2	0.1	0.2	0.0	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2		
1.7	0.1	0.1	17.6	0.1	0.2	0.1	0.2	0.0	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2		
1.8	0.1	0.1	17.6	0.1	0.2	0.1	0.2	0.0	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2		
1.9	0.1	0.1	17.6	0.1	0.2	0.1	0.2	0.0	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2		
2.0	0.1	0.1	17.6	0.1	0.2	0.1	0.2	0.0	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2		
La	0.51	0.17	0.29	0.26	0.22	0.26	0.26	0.31	0.22	0.20	0.14	0.31						
Ce	71.73	73.7	127.4	110.0	82.6	63.0	167.6	66.8	66.8	89.9	39.0	80.1						
Pr	3.74	1.32	3.02	2.30	3.87	1.39	2.64	3.25	2.64	3.25	1.51	1.18	2.63					
Nd	12.69	4.74	10.74	9.31	14.09	4.74	9.10	11.90	11.90	5.81	3.81	3.66	10.15					
Sm	54	25	51	40	63	26	50	48	50	48	30	25	46					
Eu	40	19	38	34	44	19	34	32	32	19	21	30						
Gd	19	10	19	16	19	10	16	16	16	10	15	15						
Tb	309	204	368	298	356	175	402	285	285	178	278	283						
Dy	522	363	690	550	693	323	765	485	485	359	323	512						
Ho	820	610	1095	957	955	519	1311	765	765	595	508	790						
Er	1315	1035	1711	1655	1585	879	2210	1226	1226	904	843	1275						
Tm	1769	1481	2438	2307	2108	1193	3078	1693	1693	1280	1195	1763						
Yb	2073	1791	2895	2848	2542	1486	3954	1969	1969	1450	1393	2006						
Lu	3256	2658	4422	4545	3887	2368	5860	3042	3042	2318	2234	3146						
938946	949596	984135	992212	1000665	940375	935302	998750	101215	101215	935087	959721							
98	98	98	98	98	98	98	98	98	98	98	98							
13683	16239	38946	28115	19878	12737	36178	19642	21763	21763	10143	16877							
ThU	0.77	0.60	1.03	0.69	0.75	0.67	0.77	0.77	0.77	0.84	0.64	0.80						
Yb(n)(La(n))	4025	10815	11095	11414	5651	11637	8947	7269	9835	6478	9835	6478						
Yb(n)(Gd(n))	11.2	15.8	14.3	17.3	12.3	14.3	16.9	12.0	12.6	14.1	11.8	11.8						
Yb(n)(Eu)	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4						
CoCeCo	51.6	157.7	136.3	143.3	89.0	103.8	184.2	81.4	163.9	95.9	88.7	95.9						
HClO <sub>2</sub> (Wt%)	1.2	1.2	1.2	1.2	1.2	1.2	1.1	1.2	1.1	1.2	1.1	1.2						
comment	cycles 1-7																	
main area	c1	c2	c2	c2	c1	c2	c2b	c1	c2	c2	c2a	rim						



## Appendix 2h: Zircon saturation and ‘Ti-in-zircon’ thermometry

### 1. Zircon saturation thermometry

In the past 30 years numerous studies have discussed the occurrence, stability and chemistry of zircon in crustal rocks (e.g. Baker et al., 2002; Keppler, 1993; Larsen, 1973; Maurice, 1949; Murthy, 1958; Poldervaart, 1955, 1956; Siedner, 1965; Speer, 1982; Watson, 1979). A major contribution was made by Watson (1979), who based on an experimental study concluded that in the system  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Na}_2\text{O-K}_2\text{O}$  the Zr saturation level strongly depends on the molar proportions of  $(\text{Na}_2\text{O}+\text{K}_2\text{O})/\text{Al}_2\text{O}_3$  of the melt, and only little on temperature,  $\text{SiO}_2$  content or on the ratio  $\text{Na}_2\text{O}/\text{K}_2\text{O}$ . He further determined that for peraluminous melts less than 100 ppm Zr are required to saturate the melt and crystallise zircon. In a subsequent experimental study Watson and Harrison (1983) re-investigated the relationship between zircon crystallisation, melt composition and temperature and proposed the following solubility model:

$$\ln D_{\text{Zr}}^{\text{zircon/melt}} = (-3.80 - [0.85(M-1)]) + 12900/T$$

where  $D_{\text{Zr}}^{\text{zircon/melt}}$  describes the concentration of Zr in zircon to Zr in the melt,  $M$  the cation ratio  $(\text{Na}+\text{K}+2 \text{ Ca})/(\text{Al}*\text{Si})$ , and  $T$  the temperature (in Kelvin). Based on this solubility model Watson and Harrison (1983) showed that zircon solubility is largely insensitive to pressure, deviates from the above equation only for dry ( $< \sim 1.5 \text{ wt\% H}_2\text{O}$ ) or peralkaline melts, and hence should apply to most intermediate to felsic crustal magmas. However, they also proposed that zircon solubilities vary in natural granitic systems due to the wide range of whole-rock geochemical compositions ( $M$  values), Zr concentrations and crystallisation temperatures.

Rearranging the above equation to  $T$  yields a geothermometer:

$$T_{\text{Zr}} = 12900 / [2.95 + 0.85*M + \ln (496000/\text{Zr}_{\text{melt}})]$$

However, calculated zircon saturation temperatures only give meaningful estimates, if (1) the unknown samples have  $M$  values equivalent to those used in the Watson and Harrison (1983) experiments (i.e.  $M=0.9\text{-}2.1$ ), (2) the melt was saturated in Zr,

(3) textural evidence suggests early saturation (i.e. zircons are interstitial and not predominantly located within other minerals such as micas), and (4) presence of inherited zircons suggests saturation throughout the magma's evolution.

**Table 1**  
**Zircon saturation temperatures for the Lochnagar and Etive plutons**

		Zr	M	T			Zr	M	T
		[ppm]		[°C]			[ppm]		[°C]
<b><u>Lochnagar</u></b>					<b><u>Etive</u></b>				
SA04/01	<b>AD1</b>	427	2.3	808	SA05/20	<b>MO</b>	290	1.0	870
SA04/02	<b>AD2</b>	179	2.1	744	SA05/11	<b>Cr-11</b>	124	1.7	745
SA04/13	<b>CnG</b>	230	2.4	744	SA05/17	<b>Cr-17</b>	144	1.2	788
SA04/03	<b>L1-03</b>	191	1.4	800	SA05/15	<b>Cr-15</b>	623	1.3	928
SA04/06	<b>L1-06</b>	93	1.3	748	SA05/26	<b>Cr-26</b>	457	1.2	900
SA04/04	<b>L2-04</b>	144	1.4	780	SA05/05	<b>St-05</b>	140	1.1	799
SA04/15	<b>L2-15</b>	146	1.3	784	SA05/01	<b>St-01</b>	70	1.0	749
SA04/12	<b>L2-12</b>	147	1.3	784	SA05/23	<b>Q-23</b>	121	1.6	745
SA04/05	<b>L3</b>	339	1.4	853	SA05/25	<b>Q-25</b>	143	2.1	728

For the Lochnagar pluton the calculated zircon saturation temperatures range from 744°C to 808°C (Table 1, error on the calculation = ~50°C) with a mean temperature of 783±71 °C (2SD, n=9). Samples of the Etive pluton yield a similar mean temperature of 806±150°C (2SD, n=9), but cover a larger temperature range between 728°C and 928°C. Both plutons show temperatures similar to those observed in other plutonic systems (e.g. Miller, 2003). In both plutons the majority of samples have M values within the calibrated range. However, in the Lochnagar pluton the Allt Darrarie (AD1 and AD2) and Cul nan Gad (CnG) diorites have higher M values suggesting their temperatures may not be reliable. An ambiguity affecting all the Lochnagar and Etive samples is that at present the zircons' textural relationships within the samples have not been investigated in great detail making it impossible to assess the degree of interaction between zircon and melt. In addition, only two samples in each pluton (Lochnagar: L2-04 and L2-15; Etive: Cr-15 and Cr-17) contain pre-magmatic inherited zircons, hence Zr saturation cannot be guaranteed throughout magma evolution. As further and much more detailed information is

required to eliminate these ambiguities and to calculate reliable saturation temperatures the above temperatures were not included into the main body of the text or integrated with the zircon oxygen, Hf isotope and/or REE/trace element data.

## 2. ‘Ti-in-zircon’ thermometry

Recently Watson and Harrison (2005) established that in rutile-bearing rocks the Ti content in zircon is highly dependent on temperature making it suitable as a geothermometer:

$$T(^{\circ}\text{C})_{\text{zircon}} = (5080 \pm 30 / (6.01 \pm 0.03) - \log(\text{Ti})) - 273$$

The tetravalent nature of Ti allows it to substitute into the zircon crystal lattice for  $\text{Zr}^{4+}$  or  $\text{Si}^{4+}$ . In  $\text{TiO}_2$ -saturated samples (i.e. rutile is present), the thermodynamic basis of the thermometer is the reaction  $\text{TiO}_2(\text{rutile}) = \text{TiO}_2(\text{zircon})$ . As rutile represents nearly pure  $\text{TiO}_2$  rutile-bearing rocks show a  $\text{TiO}_2$  activity that equals unity; this value decreases in rocks lacking or containing other  $\text{TiO}_2$  phases. In general, rutile predominantly occurs in metamorphic rocks, but is not common in igneous rocks. In the latter other  $\text{TiO}_2$ -bearing phases (e.g. ilmenite, titanite) constrain the  $\text{TiO}_2$  activity, which will be smaller than unity. Hence, ‘Ti-in-zircon’ temperatures calculated for igneous rocks will most likely represent minimum temperatures.

In the Lochnagar pluton the mean ‘Ti-in-zircon’ temperatures range from  $669 \pm 119^{\circ}\text{C}$  (2SD,  $n=7$ , error on calculation  $\sim 10^{\circ}\text{C}$ ) in the AD2 diorite to  $769 \pm 74^{\circ}\text{C}$  (2SD,  $n=18$ ) in the AD1 diorite (Table 2). The Etive plutons shows similar mean temperatures between  $645 \pm 62^{\circ}\text{C}$  (St-05,  $n=9$ ) and  $786 \pm 87^{\circ}\text{C}$  (Q-23,  $n=12$ ) (Table 2). Some variation occurs between each unit within the plutons. However, at least in the Lochnagar plutons this variation does not appear to be systematic. In the Etive pluton samples of the Starav Intrusion have lower ‘Ti-in-zircon’ temperatures than the Meall Odhar, Cruachan and Quarry intrusion samples. Variation also occurs between zircon crystals of a single sample as well as within individual crystals. Most commonly temperature decreases with zircon growth. However, the opposite trend can also be observed (e.g. AD1 grain 6). This may be further evidence for the

complexity of the Lochnagar and Etive plutonic systems as indicated by zircon oxygen and U-Pb isotope data. However, as the  $\text{TiO}_2$  activity has not been constrained in the Lochnagar and Etive samples temperatures are most likely underestimated and can therefore only be seen as preliminary results. In order to obtain reliable temperatures the nature and abundance of all  $\text{TiO}_2$ -bearing phases has to be constrained in great detail. As this has not been carried out at this point the temperatures were not incorporated into the main body of the thesis.

**Table 2**  
**'Ti-in-zircon' temperatures for the Lochnagar and Etive plutons**

	grain no.	analysis no.	Ti [ppm]	T [°C]	grain area		grain no.	analysis no.	Ti [ppm]	T [°C]	grain area
<b><u>Lochnagar</u></b>											
<b><u>AD1</u></b>	4	4.7	18	793	?						
	4	4.10	18	795	?						
	6	6.14	9	734	c1						
	6	6.15	21	808	c2						
	11	11.33	8	727	r1						
	11	11.34	10	738	c1a						
	14	14.43	22	815	c1						
	14	14.44	17	792	c2						
	16	16.51	11	748	c1						
	16	16.52	8	721	r3						
	8	8.20	26	832	c1						
	8	8.25	7	707	r1						
	9	9.28	14	771	c2a						
	9	9.29	11	746	c2b						
	13	13.41	16	787	c2a						
	13	13.42	9	731	c2b						
	10	10.31	18	798	c2						
	10	10.32	17	790	c1						
<b>mean</b>				<b>769</b>							
<b>2SD</b>				<b>74</b>							
<b><u>AD2</u></b>	11	11.22	10	741	c1a						
	13	13.27	2	612	c2b						
	13	13.29	2	606	c2a						
	18	18.39	12	756	rim						
	18	18.40	5	682	c1						
	15	15.32	3	643	c2b						
	15	15.31	3	644	c2a						
<b>mean</b>				<b>669</b>							
<b>2SD</b>				<b>119</b>							
<b><u>CnG</u></b>	1	1.1	12	756	c2a						
	1	1.2	5	678	c2b						
	5	5.9	8	724	c2						
	5	5.10	11	747	c1						
	6	6.14	11	750	r1						
	15	15.35	7	709	c1						
	15	15.36	5	684	r1						
	4	4.7	4	657	r1						
	4	4.8	6	699	c1						
	5	5.11	7	706	r1						
	13	13.31	5	690	c1						
	19	19.44	14	772	c1a						
	19	19.44b	14	771	c1b						
	19	19.45	8	720	r1						
<b>mean</b>				<b>719</b>							
<b>2SD</b>				<b>72</b>							
<b><u>L1-03</u></b>	3	3.6	10	744	c2a						
	3	3.57	14	770	c2b						
	8	8.14	10	745	r1						
	9	9.15	12	759	c2a						
	9	9.16	9	732	c2b						
	16	16.29	12	755	rim						
	27	27.54	15	777	c2						
	27	27.55	13	765	c1						
	12	12.19	11	746	rim						
	13	13.22	6	691	rim						
	15	15.26	7	710	c1						
	15	15.27	5	683	rim						
	22	22.42	8	724	c1						
	23	23.43	7	705	c2a						
	23	23.44	5	683	c2b						
	20	20.37	8	726	rim						
	20	20.38	11	747	c2						
	26	26.53	14	774	rim						
	24	24.46	16	786	rim						
<b>mean</b>				<b>738</b>							
<b>2SD</b>				<b>64</b>							
<b><u>L1-06</u></b>	5	5.6	13	763	c1						
	5	5.7	5	688	c2						
	7	7.10	3	642	c1						
	7	7.11	4	666	c2						
	13	13.18	14	769	c1						
	2	2.2	2	630	c1						
	30	30.36	3	645	c1						
	30	30.37	4	674	c2						
	25	35.43	6	700	c2						
	36	36.44	4	659	c1						
	36	36.45	8	719	rim						
	12	12.17	3	637	c1						
<b>mean</b>				<b>683</b>							
<b>2SD</b>				<b>94</b>							
<b><u>L2-04</u></b>	10	10.20	2	617	c1						
	10	10.21	10	738	r1						
	16	16.31	3	650	c1						
	18	18.34	7	706	c1						
	18	18.35	6	693	rim						
	11	11.22	5	688	c1						
	1	1.2	10	739	c2						
<b>mean</b>				<b>690</b>							
<b>2SD</b>				<b>89</b>							

	grain no.	analysis no.	Ti [ppm]	T [°C]	grain area		grain no.	analysis no.	Ti [ppm]	T [°C]	grain area
<b><u>L2-12</u></b>	2	2.3	5	682	c2						
	3	3.4	5	687	c2a						
	3	3.5	6	703	c2b						
	10	10.22	8	719	c2						
	11	11.25	8	723	c2						
	5	5.10	4	674	c2						
	12	12.30	12	756	c1						
	5	5.9	5	686	c1						
	13	13.33	11	746	c2						
	14	14.35	20	805	c1						
	15	15.37	4	662	c1						
	15	15.38	4	662	c2						
	11	11.26	7	705	c2						
<b>mean</b>				<b>709</b>							
<b>2SD</b>				<b>83</b>							

<b><u>L2-15</u></b>	4	4a	6	696	c2
	7	7b	7	715	rim
	9	9a	3	655	c2
	13	13a	10	743	c1
	13	13b	7	709	rim
	21	21a	7	708	c1
	21	21b	8	722	c2
	28	28a	2	625	c1
	16	16d	464	<b>1246</b>	rim
	27	27b	2	629	c1
<b>mean</b>				<b>689</b>	
<b>2SD</b>				<b>84</b>	

### **Etive**

<b><u>St-01</u></b>	4	4a	2	620	c1
	5	5b	3	648	c1
	13	13a	3	645	c2
	13	13b	4	664	rim
	18	18a	3	644	c2a
	18	18b	4	663	c2b
	19	19b	3	641	rim
	20	20a	4	659	c2
	14	14a	6	699	rim
<b>mean</b>				<b>654</b>	
<b>2SD</b>				<b>43</b>	

<b><u>L3</u></b>	21	21.40	7	708	c2
	21	21.41	6	701	rim
	14	14.27	11	746	rim
	9	9.16	9	729	c2a
	9	9.17	6	691	c2b
	25	25.49	8	719	c2b
	25	25.50	8	717	c2a
	18	18.34	7	710	c2a
	18	18.35	11	748	c2b
	28	28.56	15	777	rim
	10	10.18	5	691	c1
	4	4.7	7	709	c1+c2
	5	5.9	3	651	c1
	11	11.21	9	731	c2a
	11	11.22	6	700	c2b
	24	24.48	14	769	rim
<b>mean</b>				<b>719</b>	
<b>2SD</b>				<b>63</b>	

<b><u>St-05</u></b>	9	9a	4	658	c2
	10	10a	4	662	c2
	10	10b	5	685	rim
	11	11c	5	688	c2b
	14	14c	1	597	r1a
	14	14b	3	646	r1b
	23	23a	2	623	c2
	18	18a	2	620	c1
	18	18b	2	628	c2
<b>mean</b>				<b>645</b>	
<b>2SD</b>				<b>62</b>	

	grain no.	analysis no.	Ti [ppm]	T [°C]	grain area		grain no.	analysis no.	Ti [ppm]	T [°C]	grain area
<b>Cr-11</b>	1	1a	6	703	c1	<b>Q-23</b>	5	5a	11	749	c2
	1	1b	8	723	rim		8	8a	18	794	c2
	5	5a	11	748	c2		9	9a	22	816	c2
	5	5b	8	721	rim		10	10a	13	768	c2b
	8	8a	9	733	c2a		10	10b	19	802	c2a
	8	8b	10	738	c2b		7	7a	22	814	c1
	9	9a	12	754	c1		14	14a	21	809	c1b
	9	9b	5	686	rim		14	14c	20	807	c1a
	11	11c	11	751	c1a		16	16a	16	785	c2a
	20	20a	12	759	c2a		16	16b	14	773	c2b
	20	20d	9	732	c2d		22	22a	28	840	c1
<b>mean</b>				<b>731</b>			22	22b	4	672	c2b
<b>2SD</b>				<b>45</b>		<b>mean</b>				<b>786</b>	
						<b>2SD</b>				<b>87</b>	
<b>Cr-15</b>	2	2a	27	835	c1	<b>MO</b>	2	2a	11	752	c1
	4	4b	10	737	inh1		2	2b	10	739	c2
	9	9a	6	702	c2		6	6a	17	790	c2
	11	11a	17	787	c2a		7	7a	107	1003	c2
	11	11b	9	728	c2b		9	9a	13	764	c1
	19	19b	10	737	c2		9	9b	11	749	c2
	22	22a	10	745	c1		14	14a	13	765	c2b
	22	22b	12	757	c2		18	18a	11	749	c1
	26	26a	5	680	c1		18	18b	11	745	c2
<b>mean</b>				<b>745</b>			19	19a	12	754	c2a
<b>2SD</b>				<b>91</b>			19	19b	11	750	rim
						<b>mean</b>				<b>778</b>	
<b>Cr-26</b>	5	5a	12	755	c1	<b>2SD</b>				<b>152</b>	
	6	6a	11	751	c1						
	6	6b	9	729	c2						
	12	12a	16	782	c2b						
	16	16a	12	757	c2						
	20	20c	11	749	c1a						
	20	20b	8	719	rim						
	27	27a	7	715	c2						
<b>mean</b>				<b>745</b>							
<b>2SD</b>				<b>45</b>							

## Appendix 2i: A comparison of measured whole-rock REE data and melt compositions calculated from zircon REE data

Accessory minerals (e.g. zircon, apatite) typically make up less than one modal percent in a whole-rock sample. Nevertheless, they host the majority of trace elements and REEs useful as petrogenetic indicators (e.g. Bea, 1996; Gromet and Silver, 1983). In order to assess the controls accessory minerals have on the whole-rock REE budget back-calculations may be made from accessory mineral REE data.

For the Lochnagar and Etive plutons these calculations were made for zircon and whole-rock using the partition coefficients by Sano et al. (2002) (Table 1). The measured whole-rock and average back-calculated REE data of each sample (Tables 2 & 3) are plotted normalised to chondrite using normalising values by Sun and McDonough (1989).

In both plutons good agreement was found for the MREEs and HREEs (Fig. 1). Larger discrepancies were observed in the LREE. This may be the result of (1) the overall low LREE abundances in zircon leading to lower accuracy and reproducibility, (2) may have been caused by accidental analysis of small inclusions enriched in LREE (e.g. apatite) in zircon, (3) is evidence that other accessory minerals (e.g. apatite) provide the majority of the whole-rock's LREEs and MREEs. This comparison of measured whole-rock REE data and melt compositions calculated from zircon REE data supports the conclusion by Sano et al. (2002) that, as long as the correct zircon/melt partition coefficients are used, melt compositions may be successfully back-calculated from zircon REE data.

**Table 1**  
**Partition coefficients of REEs in zircon/melt**

Element	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
<b>zircon/melt</b>	0.0005	0.4	0.0172	0.1	0.8	1.2	8	21	46	80	136	2	277	325
<b>±</b>	0.0003	0.1	0.0088	0	0.2	0.3	1.7	4.8	9.5	19	27	40	55	62

\*data from Sano et al. (2002)



**Table 2**  
**Measured and calculated REE data for the Lochnagar pluton**

	AD1	AD1 calc	CnG	CnG calc	L1-03	L1-03 calc	L2-15	L2-15 calc	L3	L3 calc
<b>La</b>	39	237	27	865	51	12492	30	2434	63	3350
<b>Ce</b>	85	56	54	41	90	131	57	129	109	203
<b>Pr</b>	11	19	6	19	9	149	6	80	10	62
<b>Nd</b>	44	58	26	42	30	188	21	127	34	116
<b>Sm</b>	8	7	5	4	5	8	3	9	4	12
<b>Eu</b>	2.6	1.9	1.6	1.5	1.0	1.2	0.6	1.5	1.6	1.8
<b>Tb</b>	1.1	0.5	0.7	0.3	0.5	0.3	0.4	0.5	0.4	0.8
<b>Gd</b>	7.7	3.7	4.2	2.2	3.6	2.8	2.6	3.6	3.0	6.0
<b>Dy</b>	6.3	2.6	3.7	1.5	3.0	1.9	2.0	2.6	2.2	4.2
<b>Ho</b>	1.1	0.6	0.7	0.3	0.6	0.4	0.4	0.6	0.5	0.9
<b>Er</b>	2.9	1.7	2.0	1.0	1.8	1.1	1.1	1.6	1.2	2.5
<b>Tm</b>	0.5	0.3	0.3	0.2	0.3	0.2	0.2	0.2	0.2	0.4
<b>Yb</b>	2.7	1.5	1.7	1.1	1.8	1.0	1.2	1.5	1.3	2.0
<b>Lu</b>	0.4	0.3	0.2	0.2	0.3	0.2	0.2	0.3	0.2	0.4

**Table 3**  
**Measured and calculated REE data for the Etive pluton**

	MO	MO calc	Cr-11	Cr-11 calc	St-01	St-01 calc	Q-23	Q-23 calc
<b>La</b>	43	134	31	177	18	275	27	782
<b>Ce</b>	77	148	62	133	31	110	53	131
<b>Pr</b>	9	13	7	29	3	6	6	44
<b>Nd</b>	31	52	30	100	10	18	24	113
<b>Sm</b>	5	8	5	12	1	3	4	12
<b>Eu</b>	1.1	1.4	1.4	2.7	0.3	0.6	1.1	1.2
<b>Tb</b>	0.6	0.5	0.5	0.7	0.2	0.2	0.4	0.7
<b>Gd</b>	3.6	3.9	4.2	5.6	1.2	1.8	3.2	6.0
<b>Dy</b>	3.3	2.6	3.0	3.3	1.2	1.4	2.4	3.6
<b>Ho</b>	0.6	0.6	0.5	0.7	0.2	0.3	0.4	0.7
<b>Er</b>	1.7	1.6	1.3	1.9	0.7	1.0	1.2	1.9
<b>Tm</b>	0.2	0.2	0.2	0.3	0.1	0.2	0.2	0.3
<b>Yb</b>	1.5	1.3	1.2	1.6	1.0	1.1	1.2	1.5
<b>Lu</b>	0.2	0.3	0.2	0.3	0.2	0.3	0.2	0.3

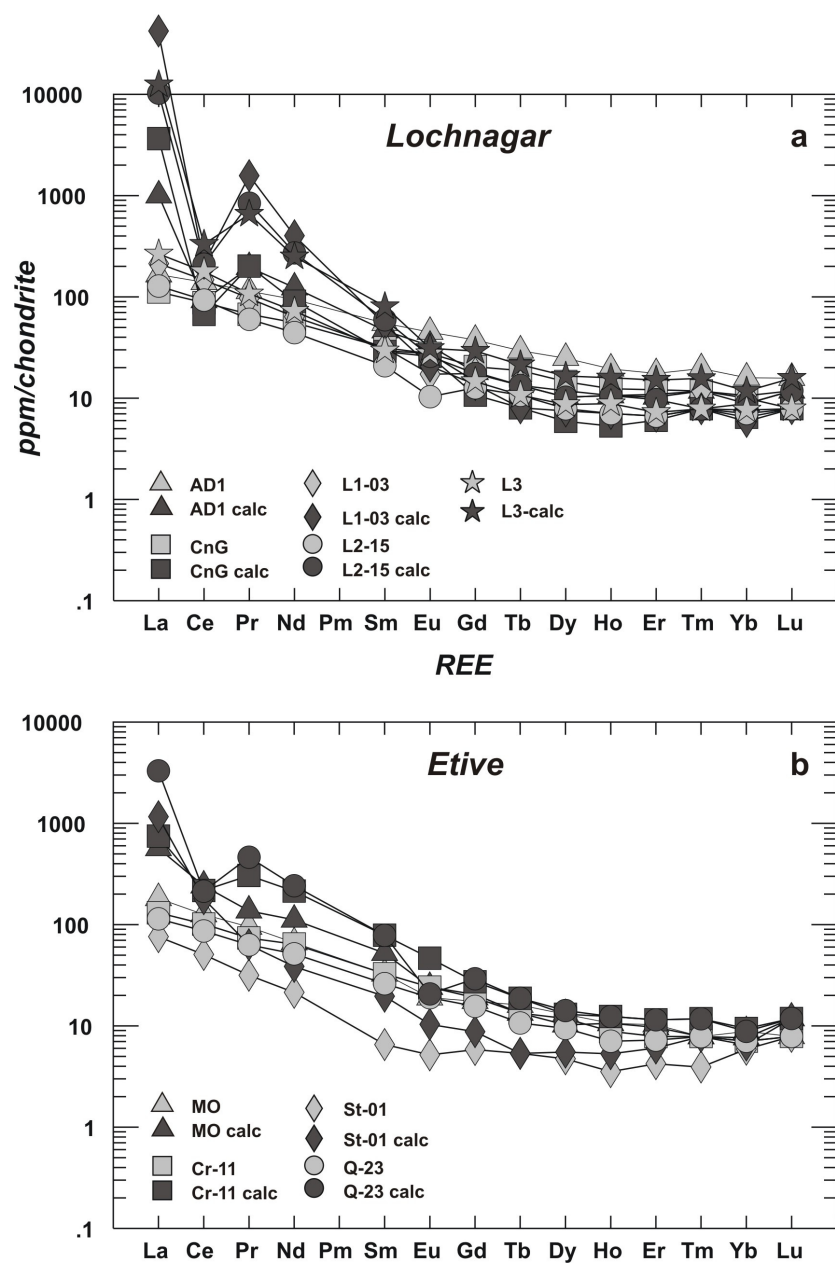


Fig. 1: Chondrite-normalised REE patterns (values from Sun and McDonough, 1989) of measured and back-calculated zircon REE data for the (a) the Lochnagar and (b) the Etive plutons.

**Appendix 2j****Two-component magma mixing modelling**

% Dalradian	$\delta^{18}\text{O}$ [‰]	% enriched mantle
0	5.5*	1
0.1	6.4	0.9
0.2	7.2	0.8
0.3	8.1	0.7
0.4	9.0	0.6
0.5	9.9	0.5
0.6	10.7	0.4
0.7	11.6	0.3
0.8	12.5	0.2
0.9	13.3	0.1
1	14.2*	0

\*Average enriched mantle and average Dalradian  
(data from Anderson et al., 2004; Eiler, 2001; Frost  
and O'Nions, 1985; O'Nions et al., 1983)

## **APPENDIX 3**

### **Supplementary data for Paper 3**

Appendix 3a  
Hf isotope data of zircons from the Lochnagar and Eltve plutons

Analysis no.	grain no.	grain area	age	1 $\sigma$	$\delta^{18}\text{O}$ [‰]	2 $\sigma$	$\frac{^{176}\text{Lu}}{^{177}\text{Hf}}$ (WR)	total Hf	Yb/Hf	$\frac{^{176}\text{Hf}}{^{177}\text{Hf}}$	1s%	$\frac{^{176}\text{Hf}}{^{177}\text{Hf}}$	1s%	$\frac{^{176}\text{Yb}}{^{177}\text{Hf}}$	1s%	$\frac{^{176}\text{Lu}}{^{177}\text{Hf}}$	1s%	$\frac{^{176}\text{Hf}}{^{177}\text{Hf}}$ (initial)	$\epsilon\text{Hf}$	95% conf.	TDM <sub>C</sub>	95% conf.	TDM <sub>W</sub>	95% conf.
<b>Lochnagar</b>																								
<b>AD1</b>																								
SA04/01 - 1.1b	1	c2	419	4	6.9	0.6	0.008	3.93	0.15	1.467270	0.0038	0.282516	0.0078	0.37217	7.5	0.00147	5.3	0.282504	-0.3	0.9	1428	53	1197	40
SA04/01 - 3.6b	3	c1	419	4	6.6	0.6	0.008	3.66	0.13	1.467130	0.0045	0.282489	0.0073	0.32758	7.6	0.00133	5.0	0.282478	-1.2	0.8	1486	50	1242	38
SA04/01 - 4.10b	4	?	419	4	7.7	0.6	0.008	3.40	0.05	1.467320	0.0047	0.282501	0.0083	0.13111	9.1	0.00055	7.0	0.282497	-0.5	0.9	1445	56	1211	42
SA04/01 - 7.17b	7	c1	419	4	7.5	0.6	0.008	4.10	0.14	1.467240	0.0048	0.282391	0.0083	0.35798	7.8	0.00132	5.0	0.282381	-4.6	0.9	1705	56	1412	42
SA04/01 - 8.20b	8	c1	419	4	6.8	0.6	0.008	2.94	0.08	1.467290	0.0060	0.282599	0.0103	0.19478	7.5	0.00084	5.4	0.282592	2.9	1.1	1230	69	1044	52
SA04/01 - 9.27b	9	c1	419	4	6.5	0.6	0.008	2.63	0.09	1.467250	0.0040	0.282614	0.0097	0.23707	7.6	0.00096	5.1	0.282606	3.4	1.1	1198	65	1020	50
SA04/01 - 9.29b	9	c2	419	4	7.3	0.6	0.008	3.24	0.06	1.467290	0.0037	0.282473	0.0078	0.15657	7.4	0.00067	4.9	0.282468	-1.6	0.9	1510	52	1261	40
SA04/01 - 10.32b	10	c1	419	4	7.8	0.6	0.008	2.98	0.08	1.467290	0.0048	0.282525	0.0113	0.20886	8.4	0.00090	6.3	0.282518	0.2	1.2	1398	75	1174	57
SA04/01 - 10.31b	10	c2	419	4	6.6	0.6	0.008	3.09	0.10	1.467230	0.0053	0.282544	0.0086	0.26180	7.4	0.00112	4.9	0.282535	0.8	1.0	1359	58	1144	44
SA04/01 - 11.34b	11	c1	419	4	7.2	0.6	0.008	4.44	0.11	1.467150	0.0064	0.282449	0.0113	0.28000	7.9	0.00114	6.2	0.282440	-2.5	1.2	1573	75	1309	57
SA04/01 - 15.49	15	c2	419	4	6.6	0.6	0.008	4.15	0.09	1.467250	0.0042	0.282384	0.0081	0.23131	7.5	0.00096	5.0	0.282376	-4.8	0.9	1715	54	1419	41
SA04/01 - 16.51b	16	c1	419	4	6.4	0.6	0.008	4.39	0.26	1.467220	0.0043	0.282511	0.0075	0.65764	7.4	0.00248	4.9	0.282491	-0.7	0.9	1457	52	1220	39
<b>CnG</b>																								
SA04/13 - 13.32	13	c2	418	6	5.7	0.4	0.007	2.82	0.03	1.467180	0.0051	0.282495	0.0092	0.06450	7.6	0.00031	5.3	0.282492	-0.7	1.1	1455	62	1193	45
SA04/13 - 14.34	14	c2	418	6	5.5	0.4	0.007	3.24	0.04	1.467310	0.0048	0.282560	0.0078	0.10874	7.5	0.00051	5.0	0.282556	1.5	0.9	1312	54	1086	39
SA04/13 - 15.35	15	c1	418	6	5.6	0.4	0.007	3.18	0.10	1.467190	0.0043	0.282545	0.0100	0.25757	7.8	0.00110	6.1	0.282536	0.9	1.2	1357	68	1119	50
SA04/13 - 16.37	16	c1	418	6	5.8	0.4	0.007	3.00	0.08	1.467190	0.0046	0.282545	0.0089	0.20330	7.6	0.00086	4.9	0.282538	0.9	1.0	1352	61	1116	44
SA04/13 - 17.39	17	c1	418	6	6.4	0.4	0.007	2.90	0.04	1.467230	0.0056	0.282575	0.0106	0.10524	9.9	0.00044	6.7	0.282571	2.1	1.2	1277	72	1060	52
SA04/13 - 19.44	19	c1	418	6	6.3	0.4	0.007	2.19	0.21	1.467190	0.0048	0.282572	0.0095	0.53290	7.4	0.00205	4.9	0.282556	1.5	1.1	1312	65	1086	47
SA04/13 - 11.28	11	c1	418	6	6.2	0.4	0.007	2.83	0.07	1.467350	0.0044	0.282584	0.0086	0.18442	7.4	0.00082	5.0	0.282577	2.3	1.0	1264	59	1050	43
SA04/13 - 9.24	9	c1	418	6	5.8	0.4	0.007	2.05	0.04	1.467310	0.0054	0.282563	0.0089	0.09790	7.6	0.00040	5.1	0.282560	1.7	1.0	1304	61	1079	44
SA04/13 - 2.4	2	c2	418	6	5.9	0.4	0.007	2.72	0.10	1.467170	0.0046	0.282581	0.0083	0.24187	7.5	0.00110	5.1	0.282572	2.1	1.0	1276	57	1058	42
SA04/13 - 4.8	4	c1	418	6	6.3	0.4	0.007	3.13	0.08	1.467300	0.0047	0.282515	0.0095	0.18998	7.9	0.00087	5.7	0.282508	-0.1	1.1	1420	64	1167	47
SA04/13 - 6.12	6	c2	418	6	5.8	0.4	0.007	3.37	0.04	1.467180	0.0049	0.282542	0.0089	0.10449	7.7	0.00051	5.3	0.282538	0.9	1.0	1353	61	1116	44
SA04/13 - 8.20	8	r1	418	6	5.8	0.4	0.007	3.15	0.05	1.467200	0.0044	0.282556	0.0078	0.12494	7.8	0.00065	5.9	0.282551	1.4	0.9	1324	54	1095	39
<b>L1-03</b>																								
SA04/03 - 3.6	3	c2	420	3	7.1	0.4	0.007	2.95	0.04	1.467190	0.0042	0.282464	0.0073	0.10446	7.4	0.00042	5.1	0.282461	-1.8	0.8	1525	48	1246	36
SA04/03 - 7.12	7	c2	420	3	6.8	0.4	0.007	3.78	0.09	1.467250	0.0052	0.282393	0.0081	0.23719	7.4	0.00088	5.3	0.282386	-4.4	0.9	1693	53	1371	39
SA04/03 - 8.14	8	r1	420	3	6.8	0.4	0.007	2.90	0.04	1.467180	0.0052	0.282450	0.0083	0.10402	8.0	0.00054	8.6	0.282446	-2.3	0.9	1559	55	1271	41
SA04/03 - 8.13	8	c1	420	3	6.8	0.4	0.007	3.24	0.10	1.467160	0.0046	0.282427	0.0081	0.25437	11.1	0.00092	8.3	0.282420	-3.2	0.9	1617	54	1315	40
SA04/03 - 9.15	9	c2	420	3	6.6	0.4	0.007	2.83	0.07	1.467320	0.0046	0.282423	0.0103	0.18585	8.0	0.00076	6.2	0.282417	-3.3	1.1	1624	68	1319	50
SA04/03 - 16.29	16	rim	420	3	6.9	0.6	0.007	3.40	0.03	1.467210	0.0046	0.282419	0.0075	0.07894	7.6	0.00031	5.3	0.282416	-3.3	0.8	1625	50	1320	37
SA04/03 - 16.28	16	c1+c2	420	3	6.9	0.6	0.007	3.86	0.13	1.467190	0.0039	0.282466	0.0078	0.31852	7.6	0.00118	5.0	0.282457	-1.9	0.9	1534	52	1253	38
SA04/03 - 20.37	20	c2	420	3	5.8	0.6	0.007	3.14	0.05	1.467270	0.0048	0.282473	0.0075	0.13395	7.7	0.00052	5.2	0.282469	-1.5	0.8	1507	50	1232	37
SA04/03 - 20.38	20	r2	420	3	6.5	0.6	0.007	2.95	0.03	1.467130	0.0042	0.282457	0.0092	0.07626	7.4	0.00031	5.2	0.282454	-2.0	1.0	1539	60	1256	44
SA04/03 - 21.41	21	r1	420	3	6.2	0.6	0.007	2.95	0.04	1.467260	0.0046	0.282464	0.0075	0.09044	7.5	0.00038	5.0	0.282461	-1.8	0.8	1525	50	1245	37
SA04/03 - 22.42	22	?	420	3	6.1	0.6	0.007	2.98	0.04	1.467280	0.0042	0.282463	0.0075	0.10724	7.4	0.00044	5.1	0.282459	-1.8	0.8	1528	50	1248	37
SA04/03 - 23.43	23	c2a	420	3	6.1	0.6	0.007	3.50	0.11	1.467190	0.0056	0.282355	0.0092	0.26479	7.5	0.00094	5.0	0.282347	-5.8	1.0	1779	60	1436	45
SA04/03 - 23.44	23	c2b	420	3	6.6	0.6	0.007	3.35	0.09	1.467240	0.0041	0.282390	0.0089	0.22958	7.5	0.00086	5.1	0.282383	-4.5	1.0	1699	59	1376	43
SA04/03 - 26.51	26	c1	420	3	7.1	0.6	0.007	2.76	0.06	1.467110	0.0062	0.282459	0.0110	0.16216	8.1	0.00061	6.1	0.282454	-2.0	1.2	1540	72	1257	53

Analysis no.	grain no.	grain area	age	1	$\delta^{18}\text{O}$	2 $\sigma$	$^{176}\text{Lu}/^{177}\text{Hf}$ (WR)	total Hf	Yb/Hf	$^{176}\text{Hf}/^{177}\text{Hf}$	1s%	$^{176}\text{Hf}/^{177}\text{Hf}$	1s%	$^{176}\text{Yb}/^{177}\text{Hf}$	1s%	$^{176}\text{Lu}/^{177}\text{Hf}$	1s%	$^{176}\text{Hf}/^{177}\text{Hf}$ (Initial)	$\epsilon\text{Hf}$	95% conf.	TDM <sub>C</sub>	95% conf.	TDM <sub>W</sub>	95% conf.
<b>L2-04</b>																								
SA04/04 - 15.28	15	c1	1046	15	6.5	0.4	0.006*	4.52	0.05	1.467190	0.0037	0.282147	0.0059	0.12311	10.6	0.00049	11.2	0.282138	0.7	0.96	1855	50	1632	32
SA04/04 - 15.29	15	c2	1046	15	6.0	0.4	0.006*	4.92	0.04	1.467270	0.0033	0.282157	0.0074	0.10438	10.7	0.00042	11.2	0.282149	1.1	1.10	1829	59	1613	38
SA04/04 - 16.31	16	c1	424	6	6.6	0.4	0.006*	5.14	0.16	1.467260	0.0051	0.282494	0.0140	0.39673	10.7	0.00147	11.4	0.282483	-0.9	1.6	1473	95	1184	67
<b>L2-15</b>																								
SA04/15 - 3a	3	c2	422	3	6.1	0.9	0.006	2.74	0.17	1.467170	0.0044	0.282587	0.0105	0.40847	12.6	0.00120	10.6	0.282578	2.4	1.2	1260	71	1029	51
SA04/15 - 4b	4	c2	422	3	6.4	0.5	0.006	3.83	0.09	1.467290	0.0046	0.282435	0.0100	0.23524	12.6	0.00070	10.6	0.282430	-2.8	1.1	1593	66	1270	47
SA04/15 - 6a	6	c1	422	3	6.0	0.9	0.006	3.12	0.03	1.467140	0.0051	0.282499	0.0098	0.07446	12.5	0.00025	10.6	0.282497	-0.4	1.1	1442	64	1160	46
SA04/15 - 12a	12	c2	422	3	7.1	0.9	0.006	3.04	0.11	1.467270	0.0050	0.282591	0.0113	0.26839	12.5	0.00086	10.6	0.282585	2.7	1.2	1245	76	1018	54
SA04/15 - 22a	22	core a	422	3	7.3	0.5	0.006	4.77	0.04	1.467030	0.0061	0.282513	0.0137	0.11013	14.1	0.00036	13.7	0.282511	0.0	1.4	1412	89	1139	64
SA04/15 - 22b	22	core b	422	3	7.5	0.5	0.006	5.19	0.23	1.467230	0.0139	0.282551	0.0271	0.58234	14.5	0.00187	11.3	0.282537	1.0	2.8	1353	178	1096	128
SA04/15 - 29a	29	inh core	1149	8	5.5	0.5	0.006	2.54	0.14	1.467040	0.0045	0.282355	0.0122	0.35307	13.9	0.00097	11.7	0.282334	10.0	1.5	1341	89	1288	62
SA04/15 - 29b	29	rim	422	3	5.5	0.5	0.006	3.35	0.13	1.467230	0.0049	0.282492	0.0103	0.33927	17.9	0.00086	14.9	0.282486	-0.9	1.1	1468	69	1180	49
SA04/15 - 36a	36	inh core	1235	19	5.2	0.5	0.006	3.27	0.11	1.467300	0.0055	0.281760	0.0105	0.27049	12.4	0.00078	10.6	0.281742	-9.1	1.5	2622	82	2240	54
SA04/15 - 32a	32	inh core	1235	19	5.7	0.5	0.006	3.54	0.07	1.467160	0.0039	0.282173	0.0125	0.18227	14.0	0.00048	12.1	0.282162	5.8	1.7	1676	95	1554	64
SA04/15 - 35b	35	inh core	1149	8	6.3	0.5	0.006	3.17	0.04	1.467240	0.0047	0.282198	0.0105	0.08883	12.6	0.00027	10.6	0.282192	4.9	1.3	1664	74	1521	51
SA04/15 - 10a	10	c2	422	3	6.6	0.9	0.006	3.67	0.07	1.467210	0.0045	0.282499	0.0113	0.18292	13.4	0.00057	11.1	0.282495	-0.5	1.2	1447	75	1164	54
																					1403	86		62
<b>L3</b>																								
SA04/05 - 8.14	8	c1+c2	423	5	7.2	0.5	0.004	5.13	0.08	1.467210	0.0061	0.282549	0.0086	0.21303	11.5	0.00081	12.0	0.282543	1.2	1.0	1339	60	1047	39
SA04/05 - 5.9	5	c1	423	5	6.3	0.5	0.004	5.77	0.11	1.467290	0.0065	0.282546	0.0119	0.27705	12.0	0.00099	13.2	0.282539	1.0	1.3	1348	81	1054	54
SA04/05 - 9.17	9	c2	423	5	6.6	0.5	0.004	4.14	0.11	1.467210	0.0038	0.282583	0.0071	0.27596	10.6	0.00112	11.2	0.282574	2.3	0.8	1267	50	999	33
SA04/05 - 11.21	11	c2	423	5	6.8	0.5	0.004	4.75	0.10	1.467200	0.0038	0.282512	0.0065	0.24876	10.6	0.00097	11.2	0.282505	-0.2	0.8	1425	46	1106	30
SA04/05 - 18.34	18	c2a	423	5	5.6	0.5	0.004	4.17	0.14	1.467240	0.0040	0.282517	0.0059	0.35386	11.4	0.00136	11.6	0.282507	-0.1	0.7	1420	43	1103	28
SA04/05 - 18.35	18	c2b	423	5	8.1	0.5	0.004	4.08	0.12	1.467220	0.0042	0.282508	0.0074	0.29035	11.1	0.00113	11.6	0.282499	-0.3	0.9	1436	52	1114	34
SA04/05 - 21.40	21	c1	423	5	6.7	0.5	0.004	5.06	0.14	1.467260	0.0042	0.282503	0.0077	0.35546	10.7	0.00141	11.2	0.282492	-0.6	0.9	1453	54	1126	36
SA04/05 - 24.48	24	c2+rim	423	5	5.6	0.5	0.004	4.03	0.06	1.467300	0.0036	0.282512	0.0083	0.13929	10.6	0.00055	11.2	0.282508	0.0	1.0	1417	57	1101	37
SA04/05 - 25.49	25	c2	423	5	6.1	0.5	0.004	3.90	0.10	1.467340	0.0041	0.282545	0.0083	0.26160	11.1	0.00110	12.0	0.282537	1.0	1.0	1353	58	1057	38
SA04/05 - 32.64	32	c1	423	5			0.004	5.50	0.13	1.467250	0.0037	0.282488	0.0065	0.32727	10.6	0.00129	11.2	0.282478	-1.1	0.8	1484	47	1147	30
<b>L1-06</b>																								
SA04/06 - 5.6	5	c1	420	4	6.8	0.5	0.004*	6.55	0.20	1.467130	0.0093	0.282509	0.0126	0.51407	11.5	0.00199	12.4	0.282494	-0.6	1.4	1451	86	1123	58
SA04/06 - 7.10	7	c1	420	4	6.5	0.5	0.004*	6.32	0.23	1.467350	0.0071	0.282562	0.0113	0.56821	11.2	0.00219	11.7	0.282545	1.2	1.3	1335	78	1044	52
SA04/06 - 18.23	18	c1+c2	420	4	5.9	0.5	0.004*	6.34	0.27	1.467370	0.0073	0.282561	0.0160	0.68749	10.7	0.00247	11.3	0.282542	1.1	1.8	1343	109	1049	73
SA04/06 - 32.46	32	c1	420	4	6.3	0.5	0.004*	3.96	0.19	1.467270	0.0042	0.282515	0.0071	0.47830	12.4	0.00169	13.0	0.282502	-0.3	0.9	1432	51	1111	34
SA04/06 - 38.49	38	c1	420	4			0.004*	5.83	0.09	1.467090	0.0055	0.282452	0.0096	0.23289	11.7	0.00092	11.7	0.282445	-2.3	1.1	1560	65	1198	43
<b>L2-12</b>																								
SA04/12 - 2.3	2	c2	419	4	6.2	0.5	0.004*	6.89	0.17	1.467220	0.0057	0.282527	0.0106	0.43366	10.6	0.00168	11.2	0.282514	0.1	1.2	1406	73	1092	49
SA04/12 - 3.4	3	c2	419	4	6.1	0.5	0.004*	5.28	0.18	1.467190	0.0051	0.282530	0.0093	0.44886	10.8	0.00180	11.3	0.282516	0.2	1.1	1401	65	1089	43
SA04/12 - 4.7	4	c2	419	4	6.2	0.5	0.004*	5.86	0.13	1.467250	0.0045	0.282531	0.0083	0.32600	11.1	0.00132	11.9	0.282521	0.3	1.0	1390	58	1082	38
SA04/12 - 5.9	5	c2	419	4	7.1	0.5	0.004*	4.76	0.19	1.467190	0.0044	0.282548	0.0059	0.47319	10.6	0.00185	11.2	0.282534	0.8	0.7	1362	44	1062	29
SA04/12 - 11.26	11	c2	419	4	6.9	0.5	0.004*	5.24	0.13	1.467250	0.0038	0.282531	0.0062	0.31881	10.7	0.00127	11.4	0.282521	0.3	0.7	1390	44	1081	29
SA04/12 - 15.38	15	c2	419	4	5.5	0.5	0.004*	6.56	0.13	1.467180	0.0056	0.282520	0.0086	0.32383	10.8	0.00132	11.3	0.282510	-0.1	1.0	1415	60	1099	40

Analysis no.	grain no.	grain area	age	1 SD [%]	$\delta^{18}\text{O}$	2 $\sigma$	$^{176}\text{Lu}/^{177}\text{Hf}$ (WR)	total Hf	Yb/Hf	$^{176}\text{Hf}/^{177}\text{Hf}$	1s%	$^{176}\text{Hf}/^{177}\text{Hf}$	1s%	$^{176}\text{Yb}/^{177}\text{Hf}$	1s%	$^{176}\text{Lu}/^{177}\text{Hf}$	$^{176}\text{Hf}/^{177}\text{Hf}$	$^{176}\text{Hf}/^{177}\text{Hf}$ (Initial)	$\epsilon\text{Hf}$	95% conf.	TDM $_{\text{C}}$	95% conf.	TDM $_{\text{W}}$	95% conf.	
Elite																									
SA05/20 - 1c	1	c2	423	3	6.2	0.5	0.005	2.75	0.08	1.467220	0.0041	0.282374	0.0103	0.21191	12.5	0.00066	10.6	0.282369	-5.0	1.11	1729	68	1341	47	
	5	c2	423	3	6.5	0.5	0.005	3.05	0.07	1.467180	0.0049	0.282416	0.0087	0.17122	12.4	0.00055	10.6	0.282412	-3.4	0.95	1633	58	1273	40	
	10	c2	423	3	6.6	0.5	0.005	3.95	0.08	1.467200	0.0037	0.282354	0.0089	0.21310	12.4	0.00065	10.6	0.282349	-5.7	0.97	1773	59	1372	41	
	14	c2	423	3	6.8	0.5	0.005	3.89	0.12	1.467210	0.0047	0.282432	0.0103	0.31326	12.7	0.00099	10.8	0.282425	-3.0	1.12	1605	69	1253	48	
	17	c1	423	3	6.8	0.5	0.005	3.88	0.08	1.467260	0.0033	0.282425	0.0103	0.20267	13.5	0.00063	11.9	0.282420	-3.1	1.11	1614	68	1260	47	
	17	c2	423	3	5.6	0.5	0.005	3.63	0.06	1.467260	0.0037	0.282382	0.0087	0.16231	12.4	0.00055	10.8	0.282378	-4.6	0.95	1709	57	1327	40	
	15	c2	423	3	6.9	0.5	0.005	3.79	0.06	1.467230	0.0041	0.282418	0.0089	0.15410	13.5	0.00050	11.4	0.282414	-3.4	0.97	1627	59	1270	41	
	13	rim	423	3	6.9	0.5	0.005	4.87	0.08	1.467270	0.0051	0.282368	0.0100	0.20715	12.4	0.00064	10.6	0.282363	-5.2	1.09	1742	66	1350	46	
	11	c1	423	3	6.2	0.5	0.005	3.99	0.08	1.467280	0.0042	0.282383	0.0089	0.20096	12.6	0.00064	10.7	0.282378	-4.6	0.97	1708	59	1326	41	
	9	c2	423	3	5.8	0.5	0.005	4.11	0.06	1.467190	0.0040	0.282359	0.0098	0.15910	12.6	0.00049	10.8	0.282355	-5.4	1.06	1759	64	1363	45	
	8	c2	423	3	6.2	0.5	0.005	4.15	0.04	1.467080	0.0037	0.282366	0.0091	0.10838	12.4	0.00034	10.6	0.282364	-5.1	0.98	1741	60	1350	41	
	6	c2	423	3	6.6	0.5	0.005	4.07	0.09	1.467160	0.0044	0.282404	0.0085	0.22009	13.0	0.00068	11.1	0.282399	-3.9	0.93	1662	57	1294	39	
SA05/11 - 2a	2	c1+c2	421	9	6.4	0.4	0.009	5.35	0.05	1.467180	0.0037	0.282319	0.0057	0.11391	11.5	0.00057	11.6	0.282315	-6.9	0.78	1851	41	1562	32	
	3	c1	421	9	6.5	0.4	0.009	5.46	0.04	1.467170	0.0038	0.282336	0.0065	0.11356	11.1	0.00052	11.5	0.282332	-6.3	0.86	1812	47	1531	36	
	7	c1+c2	421	9	6.5	0.4	0.009	6.29	0.03	1.467230	0.0054	0.282315	0.0071	0.07857	10.6	0.00039	11.2	0.282312	-7.0	0.92	1857	50	1567	39	
	8	c2	421	9	7.7	0.4	0.009	5.02	0.12	1.467270	0.0037	0.282349	0.0059	0.29645	10.6	0.00137	11.2	0.282339	-6.1	0.83	1798	44	1520	34	
	9	c1	421	9	7.5	0.4	0.009	4.93	0.11	1.467290	0.0037	0.282370	0.0065	0.27239	10.7	0.00124	11.2	0.282361	-5.3	0.88	1749	48	1481	37	
	9	c2	421	9	7.0	0.4	0.009	5.84	0.05	1.467240	0.0036	0.282334	0.0050	0.12449	10.6	0.00058	11.2	0.282330	-6.4	0.72	1818	38	1536	28	
	10	c2a	421	9	7.0	0.2	0.009	4.69	0.07	1.467230	0.0036	0.282354	0.0054	0.17041	11.1	0.00082	11.8	0.282348	-5.8	0.76	1777	40	1503	31	
	10	c2b	421	9	6.4	0.2	0.009	5.20	0.04	1.467250	0.0036	0.282340	0.0052	0.10649	11.2	0.00054	11.5	0.282336	-6.2	0.73	1804	38	1524	29	
	11	c1	421	9	7.1	0.2	0.009	4.73	0.13	1.467220	0.0047	0.282352	0.0065	0.33270	11.4	0.00146	11.8	0.282341	-6.0	0.89	1793	48	1516	37	
	11	rim	421	9	7.4	0.2	0.009	5.05	0.04	1.467220	0.0036	0.282331	0.0057	0.10151	10.7	0.00050	11.2	0.282327	-6.5	0.78	1823	41	1540	31	
	17	c2	421	9	7.3	0.4	0.009	5.40	0.08	1.467210	0.0045	0.282341	0.0059	0.19750	10.6	0.00093	11.2	0.282334	-6.2	0.81	1808	44	1528	33	
	20	c2	421	9	7.9	0.4	0.009	5.41	0.12	1.467210	0.0036	0.282316	0.0057	0.29653	10.7	0.00139	11.2	0.282305	-7.3	0.80	1872	43	1579	33	
	23	c2	421	9	7.0	0.4	0.009	5.63	0.10	1.467210	0.0034	0.282340	0.0071	0.25352	10.6	0.00122	11.3	0.282331	-6.4	0.94	1815	51	1534	40	
SA05/17 - 7b	7	rim	414	6	6.9	0.4	0.009*	5.01	0.04	1.467200	0.0046	0.282363	0.0068	0.10710	10.6	0.00051	11.4	0.282359	-5.5	0.82	1756	47	1485	37	
	8	c2	414	6	4.6	0.4	0.009*	5.89	0.05	1.467240	0.0042	0.282390	0.0083	0.12478	10.9	0.00058	11.6	0.282386	-4.6	0.98	1697	57	1437	45	
	10	c1+rim	414	6	6.7	0.4	0.009*	4.90	0.05	1.467270	0.0038	0.282357	0.0080	0.13396	10.7	0.00062	11.3	0.282353	-5.7	0.95	1771	55	1497	43	
	10	c1+rim	414	6	7.2	0.5	0.009*	4.97	0.05	1.467230	0.0051	0.282349	0.0077	0.13658	10.7	0.00060	11.2	0.282345	-6.0	0.92	1789	53	1511	41	
	13	c2	414	6	6.6	0.5	0.009*	4.64	0.04	1.467200	0.0047	0.282332	0.0057	0.10205	10.6	0.00046	11.2	0.282329	-6.6	0.71	1824	40	1539	31	
	14	c2	414	6	6.7	0.2	0.009*	4.54	0.03	1.467230	0.0040	0.282335	0.0068	0.07012	11.5	0.00034	11.8	0.282333	-6.4	0.82	1815	47	1532	36	
	17	c2	414	6	7.2	0.5	0.009*	4.18	0.05	1.467210	0.0047	0.282371	0.0071	0.12011	11.3	0.00052	11.7	0.282367	-5.2	0.86	1738	49	1471	38	
	19	rim	414	6	5.9	0.5	0.009*	4.70	0.05	1.467170	0.0042	0.282349	0.0065	0.11520	11.0	0.00049	11.3	0.282346	-6.0	0.79	1787	45	1509	35	
	20	c1+c2	414	6	7.5	0.5	0.009*	4.49	0.04	1.467210	0.0038	0.282331	0.0065	0.09837	10.7	0.00046	11.4	0.282328	-6.6	0.79	1827	45	1541	35	
	24	c2	414	6	6.2	0.5	0.009*	4.78	0.05	1.467230	0.0035	0.282345	0.0057	0.12867	10.6	0.00058	11.2	0.282341	-6.2	0.71	1797	40	1518	31	
	3	c2	414	6	6.5	0.2	0.009*	5.81	0.04	1.467170	0.0063	0.282361	0.0099	0.10660	10.9	0.00049	11.7	0.282358	-5.6	1.14	1760	67	1488	53	
	SA05/26 - 2c	2	c2	413	5	6.2	0.3	0.009*	3.21	0.05	1.46723	0.0036	0.282333	0.0095	0.13760	21.6	0.00055	20.4	0.282329	-6.6	1.1	1824	66	1539	51
		1	rim	413	5			0.009*	2.80	0.04	1.46728	0.0039	0.282352	0.0082	0.11285	21.2	0.00046	19.8	0.282349	-5.9	1.0	1780	57	1504	44
6		c1	413	5	6.1	0.3	0.009*	3.00	0.10	1.4672	0.0040	0.282324	0.0087	0.25106	21.1	0.00105	19.8	0.282316	-7.1	1.0	1853	62	1562	48	
7		c2	413	5	6.8	0.3	0.009*	2.80	0.12	1.46736	0.0038	0.282367	0.0075	0.29222	21.2	0.00118	19.9	0.282358	-5.6	0.9	1759	55	1487	43	
8		c2	413	5	6.1	0.3	0.009*	3.07	0.07	1.46732	0.0035	0.282373	0.0079	0.16583	21.1	0.00068	19.8	0.282368	-5.2	0.9	1737	56	1470	44	
11		c2	413	5	6.8	0.3	0.009*	2.92	0.07	1.46727	0.0033	0.282362	0.0098	0.16639	21.1	0.00071	19.8	0.282357	-5.6	1.1	1762	68	1490	53	
12		c2	413	5	7.6	0.3	0.009*	2.45	0.06	1.46721	0.0037	0.282351	0.0095	0.15146	21.1	0.00067	19.9	0.282346	-6.0	1.1	1786	66	1509	52	
16		c2	413	5	7.2	0.3	0.009*	2.93	0.06	1.46727	0.0039	0.282367	0.0084	0.14670	21.2	0.00062	19.9	0.282362	-5.4	1.0	1750	59	1480	46	
20		c1	413	5	6.0	0.3	0.009*	3.99	0.06	1.46733	0.0031	0.282379	0.0082	0.15531	21.3	0.00071	20.0	0.282374	-5.0	1.0	1724	58	1459	45	
27		c2	413	5	6.5	0.3	0.009*	3.58	0.10	1.46731	0.0038	0.282351	0.0077	0.09035	21.4	0.00036	20.0	0.282348	-6.0	0.9	1781	54	1505	42	
27		rim	413	5	5.3	0.3	0.009*	4.36	0.10	1.46728	0.0035	0.282353	0.0084	0.26296	21.5	0.00097	20.1	0.282346	-6.0	1.0	1787	60	1509	47	

Analysis no.	grain no.	grain area	age	1 SD [%]	$\delta^{18}\text{O}$	2 $\sigma$	$^{176}\text{Lu}/^{177}\text{Hf}$ (WR)	total Hf	Yb/Hf	$^{176}\text{Hf}/^{177}\text{Hf}$	1s%	$^{176}\text{Hf}/^{177}\text{Hf}$	1s%	$^{176}\text{Yb}/^{177}\text{Hf}$	1s%	$^{176}\text{Lu}/^{177}\text{Hf}$	$^{176}\text{Hf}/^{177}\text{Hf}$ (Initial)	$\epsilon\text{Hf}$	95% conf.	TDM <sub>C</sub>	95% conf.	TDM <sub>W</sub>	95% conf.		
SA05/15 - 4a (inh)	4	inh	1036	22	7.0	0.4	0.009*	4.47	0.04	1.467260	0.0042	0.282256	0.0079	0.09480	21.2	0.00039	19.8	0.282249	4.4	1.33	1611	73	1494	52	
	8	inh	1646	6	5.9	0.4	0.009*	4.10	0.05	1.467260	0.0033	0.281749	0.0080	0.12292	21.2	0.00053	19.8	0.281733	-0.1	1.04	2374	75	2227	55	
	11	c2	413	5	6.3	0.4	0.009*	3.44	0.08	1.467320	0.0043	0.282407	0.0090	0.19225	21.2	0.00085	19.8	0.282401	-4.1	1.05	1664	62	1411	49	
	19	c1	413	5	6.9	0.4	0.009*	2.49	0.05	1.467260	0.0045	0.282383	0.0101	0.13428	21.5	0.00059	19.9	0.282379	-4.8	1.15	1713	68	1450	54	
	22	c1+c2	413	5	6.8	0.4	0.009*	2.94	0.06	1.467250	0.0043	0.282413	0.0082	0.14185	21.2	0.00064	19.8	0.282408	-3.8	0.96	1647	57	1397	44	
	25	c2+rim	413	5	5.7	0.4	0.009*	3.67	0.05	1.467310	0.0036	0.282350	0.0087	0.13485	21.2	0.00064	19.9	0.282345	-6.0	1.01	1788	60	1510	47	
	29	c2	413	5	5.3	0.4	0.009*	3.21	0.05	1.467280	0.0038	0.282333	0.0079	0.11945	21.2	0.00049	19.8	0.282329	-6.6	0.93	1823	55	1539	43	
	26	c1+c2	413	5	5.9	0.4	0.009*	5.13	0.07	1.467260	0.0032	0.282366	0.0073	0.17216	21.1	0.00083	19.8	0.282360	-5.5	0.88	1755	52	1484	40	
	15	c2	413	5	6.2	0.4	0.009*	2.98	0.09	1.467240	0.0032	0.282381	0.0084	0.21755	21.2	0.00096	19.9	0.282374	-5.0	1.00	1724	59	1459	46	
	3	c1	413	5	6.3	0.4	0.009*	3.22	0.12	1.467110	0.0048	0.282391	0.0118	0.30769	21.1	0.00115	19.8	0.282382	-4.7	1.35	1705	81	1444	64	
SA05/05 - 4a	4	c2	412	6	7.2	0.4	0.008*	6.15	0.07	1.467250	0.0036	0.282290	0.0074	0.18907	10.6	0.00099	11.2	0.282283	-8.3	0.90	1928	52	1583	39	
	9	c2+rim	412	6	6.9	0.4	0.008*	6.74	0.11	1.467200	0.0041	0.282275	0.0062	0.27014	11.3	0.00138	12.0	0.282265	-8.9	0.79	1968	45	1614	34	
	11	rim	412	6	7.1	0.4	0.008*	7.45	0.03	1.467230	0.0046	0.282278	0.0057	0.06728	10.8	0.00039	11.2	0.282275	-8.5	0.71	1945	40	1596	30	
SA05/01 - 6a	6	c2	408	6	7.0	0.6	0.008	6.47	0.10	1.467220	0.0044	0.282293	0.0059	0.25028	10.7	0.00123	11.3	0.282284	-8.3	0.76	1928	43	1582	32	
	5	c1+c2	408	6	7.4	0.6	0.008	7.11	0.06	1.467170	0.0039	0.282266	0.0059	0.15473	10.8	0.00077	11.6	0.282260	-9.1	0.75	1980	42	1622	31	
	7	c2	408	6	7.2	0.6	0.008	6.98	0.04	1.467220	0.0045	0.282255	0.0057	0.11092	10.7	0.00056	11.2	0.282251	-9.5	0.71	2001	40	1638	30	
	8	c1	408	6	7.1	0.6	0.008	6.49	0.04	1.467220	0.0042	0.282284	0.0065	0.10581	10.7	0.00055	11.3	0.282280	-8.4	0.80	1936	45	1588	34	
	9	c1	408	6	7.0	0.4	0.008	4.96	0.11	1.467210	0.0037	0.282229	0.0062	0.28582	11.4	0.00129	12.3	0.282219	###	0.79	2071	45	1693	33	
	14	rim	408	6	7.0	0.4	0.008	5.91	0.08	1.467270	0.0043	0.282273	0.0057	0.19611	10.6	0.00097	11.3	0.282266	-8.9	0.72	1968	41	1613	30	
	18	c2+rim	408	6	6.7	0.4	0.008	5.59	0.05	1.467250	0.0049	0.282250	0.0074	0.13544	10.9	0.00065	11.7	0.282245	-9.7	0.89	2014	51	1648	38	
	18	rim+c2	408	6	6.6	0.4	0.008	6.07	0.04	1.467170	0.0042	0.282259	0.0059	0.10556	10.6	0.00058	11.2	0.282255	-9.3	0.74	1992	42	1632	31	
	19	rim	408	6	6.5	0.4	0.008	6.11	0.04	1.467210	0.0057	0.282278	0.0065	0.09172	10.7	0.00051	11.2	0.282274	-8.6	0.79	1949	45	1598	34	
	20	c2	408	6	7.1	0.4	0.008	5.85	0.05	1.467180	0.0051	0.282267	0.0062	0.12736	11.2	0.00062	11.4	0.282263	-9.1	0.77	1975	44	1619	32	
SA05/23 - 1a	1	c1	408	4	5.9	0.3	0.007	3.34	0.12	1.467080	0.0045	0.282344	0.0104	0.29991	21.1	0.00108	19.8	0.282336	-6.5	1.18	1812	71	1458	52	
	5	c2	408	4	6.2	0.3	0.007	4.00	0.15	1.467410	0.0079	0.282385	0.0134	0.36980	21.2	0.00134	19.8	0.282375	-5.1	1.50	1725	91	1392	67	
	6	c2	408	4	5.5	0.3	0.007	3.83	0.10	1.467500	0.0054	0.282330	0.0118	0.24101	21.3	0.00085	20.0	0.282324	-6.9	1.32	1839	80	1478	59	
	10	c2	408	4	6.5	0.3	0.007	4.34	0.08	1.467320	0.0048	0.282377	0.0098	0.21192	21.2	0.00085	19.9	0.282371	-5.2	1.11	1734	67	1399	49	
	11	c2	408	4	6.1	0.3	0.007	3.80	0.08	1.467280	0.0040	0.282364	0.0087	0.19851	21.6	0.00090	20.1	0.282357	-5.7	1.00	1764	60	1422	44	
	15	c1	408	4	5.9	0.3	0.007	3.55	0.03	1.467240	0.0039	0.282351	0.0092	0.08658	21.1	0.00039	19.8	0.282348	-6.0	1.03	1784	62	1437	45	
SA05/23 - 15a	16	c2	408	4	6.7	0.3	0.007	3.92	0.08	1.467240	0.0040	0.282350	0.0077	0.20446	21.5	0.00098	19.9	0.282343	-6.2	0.91	1797	54	1446	40	
	22	c1	408	4	6.7	0.3	0.007	2.85	0.03	1.467300	0.0037	0.282384	0.0084	0.07854	21.1	0.00033	19.8	0.282382	-4.8	0.95	1710	57	1381	42	
	SA05/25 - 4a	4	c2	405	12	5.9	0.3	0.007*	3.84	0.14	1.467090	0.0055	0.282331	0.0131	0.34746	21.5	0.00142	19.8	0.282320	-7.1	1.64	1848	94	1484	67
		6	c2	405	12	6.5	0.3	0.007*	2.78	0.11	1.467230	0.0047	0.282403	0.0125	0.28364	21.7	0.00108	19.9	0.282395	-4.4	1.56	1682	89	1359	64
9		c1	405	12	5.6	0.3	0.007*	1.94	0.08	1.467350	0.0050	0.282401	0.0128	0.21122	22.7	0.00088	21.4	0.282395	-4.4	1.58	1683	91	1360	65	
10		c2	405	12	4.9	0.3	0.007*	2.53	0.19	1.467290	0.0112	0.282565	0.0134	0.47931	21.7	0.00167	19.9	0.282553	1.1	1.68	1328	97	1094	70	
16		c2	405	12	6.1	0.3	0.007*	3.94	0.07	1.467260	0.0049	0.282415	0.0101	0.18452	21.9	0.00076	20.5	0.282410	-3.9	1.31	1649	73	1335	52	
24		c2	405	12	6.9	0.3	0.007*	3.11	0.14	1.467270	0.0048	0.282384	0.0092	0.35801	21.2	0.00154	19.9	0.282373	-5.2	1.25	1732	70	1397	49	
SA05/25 - 24b	24	c2	405	12	6.3	0.3	0.007*	3.18	0.16	1.467200	0.0035	0.282415	0.0087	0.40569	21.1	0.00162	19.8	0.282403	-4.2	1.20	1664	67	1346	47	

c1 = unzoned inner core

c2 = oscillatory zoned outer core

r1-2 = rim

\* $^{176}\text{Lu}/^{177}\text{Hf}$  (WR) ratio not calculated based on the Lu/Hf ratio of the whole-rock; assumed to be similar to other samples of same mapped unit showing the same  $\epsilon\text{Hf}$  value



Appendix 3b  
Hf isotope data of Mud Tank zircon standard

	total Hf	1σ	Yb/Hf	1σ	<sup>176</sup> Yb/ <sup>177</sup> Hf	1σ	<sup>176</sup> Lu/ <sup>177</sup> Hf	1σ	<sup>176</sup> Hf/ <sup>177</sup> Hf	1σ
13/12/06										
mud tank 1	5.1	0.10	0.004	0.000021	0.011160	0.000053	0.0002361	0.0000006	0.282506	0.000010
mud tank 2	5.1	0.11	0.004	0.000017	0.011142	0.000042	0.0002357	0.0000006	0.282491	0.000020
mud tank 3	5.0	0.12	0.004	0.000014	0.011173	0.000036	0.0002362	0.0000006	0.282500	0.000011
mud tank 4	4.8	0.12	0.004	0.000013	0.011376	0.000034	0.0002417	0.0000007	0.282496	0.000015
mud tank 5	4.6	0.11	0.005	0.000013	0.012351	0.000032	0.0002621	0.0000006	0.282507	0.000013
mud tank 6	4.8	0.11	0.005	0.000012	0.012265	0.000032	0.0002617	0.0000006	0.282468	0.000016
mud tank 7	4.8	0.11	0.004	0.000014	0.010731	0.000035	0.0002302	0.0000009	0.282471	0.000015
mud tank 8	5.0	0.11	0.005	0.000015	0.011413	0.000039	0.0002419	0.0000007	0.282500	0.000016
Mud tank 9	4.6	0.08	0.004	0.000014	0.010985	0.000036	0.0002305	0.0000008	0.282468	0.000011
Mud tank 10	4.6	0.08	0.004	0.000018	0.010848	0.000045	0.0002237	0.0000007	0.282489	0.000014
Mud tank 11	4.9	0.08	0.004	0.000021	0.010938	0.000053	0.0002355	0.0000006	0.282480	0.000015
Mud tank 12	4.7	0.07	0.004	0.000022	0.010834	0.000055	0.0002290	0.0000007	0.282484	0.000011
Mud tank 13	4.5	0.07	0.004	0.000018	0.010878	0.000045	0.0002259	0.0000007	0.282489	0.000011
Mud tank 14	4.4	0.06	0.004	0.000020	0.010882	0.000050	0.0002262	0.0000005	0.282479	0.000016
Mud Tank 15	4.3	0.06	0.004	0.000014	0.011049	0.000035	0.0002249	0.0000005	0.282476	0.000012
Mud Tank 16	4.7	0.06	0.004	0.000017	0.011119	0.000043	0.0002244	0.0000004	0.282473	0.000010
Mud Tank 17	4.2	0.05	0.004	0.000022	0.009601	0.000054	0.0002182	0.0000006	0.282465	0.000017
Mud Tank 18	4.3	0.07	0.004	0.000019	0.009433	0.000047	0.0002171	0.0000006	0.282470	0.000013
Mud Tank 19	4.3	0.07	0.004	0.000021	0.009833	0.000052	0.0002323	0.0000007	0.282491	0.000017
Mud Tank 20	4.3	0.07	0.004	0.000022	0.009699	0.000055	0.0002258	0.0000005	0.282477	0.000012
Mud Tank 21	4.1	0.06	0.004	0.000019	0.009767	0.000049	0.0002307	0.0000008	0.282492	0.000012
Mud Tank 22	3.9	0.05	0.004	0.000023	0.009857	0.000057	0.0002310	0.0000006	0.282523	0.000018
14/12/06										
Mud tank 1	4.5	0.07	0.004	0.000024	0.010034	0.000061	0.0002261	0.0000006	0.282521	0.000018
Mud tank 2	4.2	0.09	0.005	0.000031	0.011716	0.000077	0.0002588	0.0000007	0.282512	0.000012
Mud tank 3	4.2	0.10	0.004	0.000025	0.010480	0.000064	0.0002376	0.0000007	0.282526	0.000012
Mud tank 4	3.9	0.10	0.005	0.000026	0.011611	0.000065	0.0002580	0.0000007	0.282530	0.000015
Mud tank 5	4.3	0.11	0.004	0.000028	0.009822	0.000070	0.0002259	0.0000009	0.282483	0.000014
Mud tank 6	4.3	0.11	0.004	0.000020	0.010564	0.000051	0.0002402	0.0000007	0.282505	0.000016
Mud Tank 7	4.2	0.10	0.005	0.000024	0.012785	0.000061	0.0002913	0.0000006	0.282496	0.000019
Mu Tank 8	4.1	0.09	0.005	0.000033	0.012129	0.000084	0.0002767	0.0000008	0.282473	0.000015
Mud Tank 9	3.9	0.08	0.004	0.000020	0.009684	0.000051	0.0002143	0.0000006	0.282499	0.000010
Mud tank 10	4.0	0.08	0.005	0.000025	0.011990	0.000063	0.0002432	0.0000007	0.282475	0.000009
Mud tank 11	4.2	0.09	0.004	0.000021	0.011072	0.000053	0.0002289	0.0000008	0.282511	0.000011
Mud Tank 12	4.5	0.09	0.006	0.000017	0.014095	0.000044	0.0002946	0.0000008	0.282510	0.000012
Mud Tank 13	4.5	0.10	0.006	0.000018	0.014799	0.000046	0.0003048	0.0000006	0.282518	0.000011
Mud Tank 14	4.4	0.10	0.006	0.000023	0.014029	0.000058	0.0002912	0.0000008	0.282509	0.000015
Mud Tank 15	3.9	0.08	0.005	0.000027	0.013356	0.000069	0.0002685	0.0000006	0.282470	0.000019
Mud Tank 16	3.7	0.06	0.004	0.000022	0.011311	0.000056	0.0002248	0.0000008	0.282544	0.000021
Mud Tank 17	4.5	0.10	0.005	0.000021	0.013512	0.000053	0.0002609	0.0000006	0.282486	0.000014
Mud Tank 18	4.6	0.09	0.005	0.000023	0.011856	0.000059	0.0002322	0.0000005	0.282498	0.000013
Mud Tank 19	4.7	0.10	0.005	0.000028	0.012116	0.000072	0.0002408	0.0000007	0.282517	0.000012
Mud Tank 20	4.6	0.11	0.005	0.000021	0.012959	0.000051	0.0002510	0.0000005	0.282490	0.000015
15/12/06										
Mud Tank 1	4.2	0.11	0.005	0.000023	0.011431	0.000059	0.0002110	0.0000006	0.282525	0.000012
Mud Tank 2	4.2	0.11	0.005	0.000016	0.011759	0.000040	0.0002154	0.0000006	0.282512	0.000016
Mud Tank 3	4.2	0.10	0.004	0.000024	0.011171	0.000061	0.0002062	0.0000006	0.282506	0.000016
Mud Tank 4	4.3	0.11	0.005	0.000023	0.011675	0.000058	0.0002131	0.0000006	0.282521	0.000016
Mud Tank 5	4.6	0.08	0.004	0.000035	0.010439	0.000087	0.0001952	0.0000006	0.282502	0.000016
Mud Tank 6	4.6	0.10	0.004	0.000029	0.010255	0.000073	0.0001896	0.0000004	0.282496	0.000015
Mud Tank 7	4.2	0.10	0.004	0.000021	0.010795	0.000053	0.0001937	0.0000006	0.282518	0.000010
Mud Tank 8	4.1	0.10	0.005	0.000025	0.011456	0.000062	0.0002132	0.0000007	0.282512	0.000018
Mud Tank 9	4.6	0.09	0.004	0.000034	0.010616	0.000086	0.0002143	0.0000005	0.282514	0.000015
Mud Tank 10	4.4	0.08	0.004	0.000031	0.010665	0.000077	0.0002070	0.0000005	0.282495	0.000016
Mud Tank 11	4.0	0.09	0.004	0.000028	0.011202	0.000070	0.0002035	0.0000006	0.282499	0.000013
Mud Tank 12	4.0	0.10	0.004	0.000037	0.011085	0.000093	0.0002024	0.0000005	0.282517	0.000018
Mud Tank 13	3.8	0.08	0.004	0.000028	0.010938	0.000070	0.0002069	0.0000008	0.282505	0.000016
Mud Tank 14	3.8	0.06	0.004	0.000035	0.010800	0.000089	0.0002007	0.0000006	0.282510	0.000015
Mud Tank 15	5.4	0.11	0.004	0.000017	0.009333	0.000044	0.0001994	0.0000005	0.282524	0.000015
Mud Tank 16	5.3	0.11	0.005	0.000022	0.013619	0.000056	0.0002869	0.0000007	0.282493	0.000013
Mud Tank 17	5.0	0.10	0.005	0.000041	0.013523	0.000100	0.0002764	0.0000005	0.282510	0.000012
Mud Tank 18	5.6	0.10	0.004	0.000026	0.009330	0.000066	0.0001970	0.0000004	0.282516	0.000014
Mud Tank 19	5.6	0.11	0.004	0.000023	0.009149	0.000058	0.0001957	0.0000004	0.282497	0.000010
Mud Tank 20	5.4	0.11	0.004	0.000027	0.010034	0.000068	0.0002185	0.0000006	0.282501	0.000014
Mud Tank 21	5.1	0.11	0.004	0.000028	0.009546	0.000071	0.0002083	0.0000006	0.282496	0.000012
Mud Tank 22	5.1	0.10	0.004	0.000025	0.010261	0.000063	0.0002171	0.0000006	0.282517	0.000013
Mud Tank 23	5.0	0.12	0.004	0.000029	0.010007	0.000072	0.0002113	0.0000006	0.282497	0.000012
Mud Tank 24	6.3	0.12	0.004	0.000019	0.010792	0.000048	0.0002332	0.0000004	0.282526	0.000012
Mud Tank 25	5.1	0.11	0.005	0.000030	0.011935	0.000076	0.0002383	0.0000006	0.282520	0.000011
Mud Tank 26	4.9	0.11	0.005	0.000033	0.011741	0.000083	0.0002323	0.0000006	0.282525	0.000013
Mud Tank 27	5.0	0.11	0.004	0.000022	0.009070	0.000054	0.0001769	0.0000004	0.282507	0.000013
average (n=69)	4.6		0.004417		0.011158		0.000231		0.282500	
2SD	1.0		0.000986		0.002515		0.000054		0.000036	

	total Hf	1 $\sigma$	Yb/Hf	1 $\sigma$	<sup>176</sup> Yb/ <sup>177</sup> Hf	1 $\sigma$	<sup>176</sup> Lu/ <sup>177</sup> Hf	1 $\sigma$	<sup>176</sup> Hf/ <sup>177</sup> Hf	1 $\sigma$
<b>07/02/07</b>										
Mud Tank 1	4.6	0.10	0.005	0.000019	0.012201	0.000047	0.0002353	0.0000009	0.282540	0.000014
Mud Tank 2	5.3	0.09	0.005	0.000028	0.012417	0.000071	0.0002389	0.0000006	0.282519	0.000013
Mud Tank 3	4.9	0.12	0.005	0.000018	0.011950	0.000044	0.0002322	0.0000005	0.282509	0.000012
Mud Tank 4	4.9	0.11	0.005	0.000018	0.011886	0.000045	0.0002251	0.0000007	0.282484	0.000010
Mud Tank 5	5.1	0.11	0.005	0.000022	0.013796	0.000056	0.0002575	0.0000006	0.282515	0.000012
Mud Tank 6	5.0	0.09	0.006	0.000029	0.014386	0.000074	0.0002678	0.0000008	0.282537	0.000009
Mud Tank 7	4.7	0.05	0.002	0.000015	0.005273	0.000038	0.0001138	0.0000007	0.282519	0.000014
Mud Tank 8	4.5	0.05	0.003	0.000020	0.006572	0.000049	0.0001482	0.0000006	0.282499	0.000012
Mud Tank 9	4.1	0.05	0.003	0.000017	0.006295	0.000044	0.0001374	0.0000006	0.282489	0.000012
Mud Tank 10	3.6	0.04	0.004	0.000018	0.008921	0.000044	0.0001936	0.0000009	0.282525	0.000019
Mud Tank 11	5.2	0.06	0.004	0.000030	0.011259	0.000076	0.0002182	0.0000009	0.282504	0.000016
Mud Tank 12	5.0	0.04	0.005	0.000040	0.011808	0.000100	0.0002242	0.0000005	0.282477	0.000008
Mud Tank 13	5.2	0.09	0.005	0.000022	0.011457	0.000055	0.0002248	0.0000005	0.282537	0.000012
Mud Tank 14	4.5	0.08	0.005	0.000019	0.012323	0.000047	0.0002356	0.0000006	0.282515	0.000014
Mud Tank 15	4.7	0.09	0.005	0.000028	0.011898	0.000070	0.0002270	0.0000006	0.282517	0.000010
Mud Tank 16	4.7	0.08	0.005	0.000026	0.013125	0.000066	0.0002512	0.0000006	0.282484	0.000009
Mud Tank 17	4.6	0.08	0.005	0.000025	0.012249	0.000064	0.0002357	0.0000006	0.282515	0.000013
Mud Tank 18	4.8	0.08	0.005	0.000034	0.011919	0.000084	0.0002247	0.0000006	0.282496	0.000011
Mud Tank 19	4.7	0.10	0.005	0.000029	0.011839	0.000072	0.0002294	0.0000007	0.282511	0.000011
Mud Tank 20	4.3	0.09	0.004	0.000020	0.010578	0.000049	0.0002246	0.0000006	0.282500	0.000014
Mud Tank 21	4.4	0.09	0.004	0.000022	0.010775	0.000055	0.0002321	0.0000006	0.282531	0.000015
Mud Tank 22	4.1	0.10	0.004	0.000018	0.011108	0.000046	0.0002271	0.0000007	0.282505	0.000013
<b>08/02/07</b>										
Mud Tank 1	5.9	0.06	0.007	0.000052	0.017588	0.000130	0.0002956	0.0000006	0.282508	0.000012
Mud Tank 2	6.0	0.07	0.007	0.000043	0.017752	0.000110	0.0003006	0.0000003	0.282486	0.000010
Mud Tank 3	6.2	0.11	0.007	0.000035	0.017047	0.000088	0.0002987	0.0000006	0.282514	0.000012
Mud Tank 4	6.2	0.10	0.007	0.000030	0.016695	0.000075	0.0002905	0.0000005	0.282513	0.000012
Mud Tank 5	6.2	0.11	0.007	0.000038	0.017507	0.000095	0.0003028	0.0000006	0.282498	0.000010
Mud Tank 6	4.9	0.10	0.007	0.000034	0.018183	0.000085	0.0003054	0.0000005	0.282515	0.000010
Mud Tank 7	5.3	0.10	0.007	0.000034	0.017745	0.000086	0.0003025	0.0000005	0.282499	0.000012
Mud Tank 8	4.5	0.07	0.007	0.000041	0.018170	0.000100	0.0003037	0.0000006	0.282492	0.000012
Mud Tank 9	4.9	0.09	0.007	0.000044	0.018256	0.000110	0.0003046	0.0000005	0.282486	0.000010
Mud Tank 10	4.7	0.09	0.007	0.000032	0.017485	0.000081	0.0002925	0.0000007	0.282537	0.000013
Mud Tank 11	5.2	0.09	0.007	0.000036	0.016926	0.000091	0.0002910	0.0000005	0.282518	0.000012
Mud Tank 12	5.1	0.06	0.008	0.000060	0.019555	0.000150	0.0003241	0.0000008	0.282527	0.000013
Mud Tank 13	5.5	0.06	0.008	0.000040	0.019314	0.000099	0.0003218	0.0000006	0.282506	0.000013
Mud Tank 14	4.7	0.08	0.008	0.000079	0.019078	0.000200	0.0003131	0.0000007	0.282513	0.000013
Mud Tank 15	5.4	0.06	0.007	0.000051	0.018439	0.000130	0.0003052	0.0000007	0.282512	0.000010
Mud Tank 16	5.7	0.05	0.007	0.000053	0.017897	0.000130	0.0002976	0.0000005	0.282510	0.000011
Mud Tank 17	5.8	0.06	0.005	0.000040	0.013722	0.000100	0.0002295	0.0000006	0.282505	0.000009
Mud Tank 18	6.1	0.13	0.006	0.000042	0.015670	0.000110	0.0002612	0.0000007	0.282535	0.000011
Mud Tank 19	6.1	0.13	0.007	0.000051	0.017408	0.000130	0.0002881	0.0000005	0.282509	0.000012
Mud Tank 20	6.1	0.10	0.006	0.000047	0.016142	0.000120	0.0002672	0.0000005	0.282521	0.000009
Mud Tank 21	5.9	0.05	0.007	0.000052	0.016741	0.000130	0.0002779	0.0000005	0.282530	0.000013
Mud Tank 22	5.5	0.06	0.007	0.000052	0.016853	0.000130	0.0002804	0.0000008	0.282513	0.000011
Mud Tank 23	5.2	0.08	0.007	0.000058	0.017852	0.000150	0.0002953	0.0000006	0.282511	0.000016
Mud Tank 24	4.6	0.08	0.007	0.000062	0.017262	0.000160	0.0002815	0.0000008	0.282540	0.000014
Mud Tank 25	5.3	0.09	0.006	0.000030	0.015944	0.000076	0.0002574	0.0000005	0.282508	0.000010
Mud Tank 26	5.7	0.10	0.007	0.000033	0.017936	0.000082	0.0002951	0.0000004	0.282525	0.000012
average (n=48)	5.1		0.005761		0.014525		0.000258		0.282512	
2SD	1.3		0.002869		0.007246		0.000093		0.000031	

### Appendix 3c: Hf isotope methodology – Correction for isobaric Yb interference

In order to obtain accurate  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios for zircons corrections for the interference of  $^{176}\text{Lu}$  and  $^{176}\text{Yb}$  on  $^{176}\text{Hf}$  have to be carried out. These may be made by monitoring the signal intensities of the interference-free isotopes  $^{175}\text{Lu}$  and  $^{173}\text{Yb}$ ,  $^{172}\text{Yb}$  or  $^{171}\text{Yb}$ , which are used to calculate the intensities for  $^{176}\text{Lu}$  and  $^{176}\text{Yb}$ . At the NERC Isotope Geosciences Laboratory (NIGL) in Nottingham corrections were applied based on the signal intensities of  $^{175}\text{Lu}$  using the  $^{176}\text{Lu}/^{175}\text{Lu}$  ratio of 0.02653 and  $^{173}\text{Yb}$ . The appropriate value of  $^{176}\text{Yb}/^{173}\text{Yb}$  (0.79488) was determined by successively spiking the JMC475 Hf standard with Yb. This method of Yb correction has been shown to provide accurate Hf isotope data, if the difference between the Yb mass bias factor ( $\beta(\text{Yb})$ ) and Hf mass bias factor ( $\beta(\text{Hf})$ ) is constant between different samples (solution standard and zircon) (Thirlwall and Walder, 1995; Griffin et al., 2000, 2002, 2004; Andersen et al., 2002; Andersen and Griffin, 2004). However, Iziuka and Hirata (2005) demonstrated by analysing a mixed solution of Hf standard JMC475 and Yb standard Cica-Merck, and solid samples of NIST SRM 610 glass and zircon standard 91500 that data from all samples deviate from the line  $\beta(\text{Yb}) = \beta(\text{Hf})$  indicating that  $\beta(\text{Yb})$  must be determined separately from  $\beta(\text{Hf})$ . In addition, they found that both  $\beta(\text{Yb})$  and  $\beta(\text{Hf})$  changed with analysis time, and that all samples formed different regression lines with differing slopes. Based on these results they suggested that  $\beta(\text{Yb})$  based on solution data cannot be applied to in-situ Hf isotope analysis of zircons.

At NIGL a peak jumping routine including  $^{172}\text{Yb}$  to allow assessment of the effect of using a Yb mass bias correction for the Yb interference correction in addition to a Hf mass bias correction, has been investigated but was nevertheless found unnecessary with the data for both being equivalent within the increased uncertainty reflected by the low Yb concentrations. Therefore, the Yb interference correction was solely based on solution data. To illustrate the appropriateness of this correction method the measured  $^{176}\text{Hf}/^{177}\text{Hf}$  and  $^{176}\text{Yb}/^{177}\text{Hf}$  ratios determined on all unknown zircons are plotted (Fig. 1). This shows that as no positively sloping trend can be observed, correctness of the method may be assumed. Supporting evidence is

that Yb-doped JMC475 solutions gave  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios indistinguishable of undoped solutions (Table 1) and within analytical uncertainty (2SD) of the accepted value of JMC475 ( $^{176}\text{Hf}/^{177}\text{Hf} = 0.28216$  (Nowell et al., 1998)).

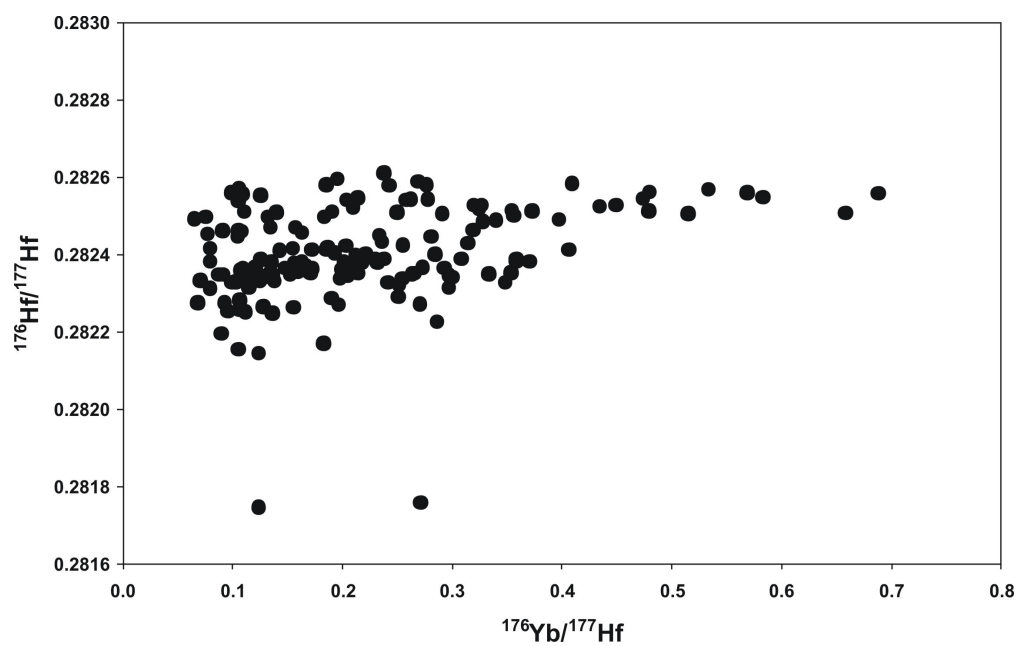


Fig. 1:  $^{176}\text{Yb}/^{177}\text{Hf}$  vs.  $^{176}\text{Hf}/^{177}\text{Hf}$  plot demonstrating the correctness of the Yb interference method.

Table 1  
Hf isotope data of undoped and doped JMC475 solution standard

	total Hf	1 $\sigma$	Yb/Hf	1 $\sigma$	$^{176}\text{Yb}/^{177}\text{Hf}$	1 $\sigma$	$^{176}\text{Lu}/^{177}\text{Hf}$	1 $\sigma$	$^{176}\text{Hf}/^{177}\text{Hf}$	1 $\sigma$
<b>13/12/06</b>										
JMC475 - undoped	11.9	0.02	0.000	0.000001	-0.000023	0.000003	-0.0000001	0.0000001	0.282143	0.000004
JMC475 - undoped	12.0	0.02	0.000	0.000001	-0.000021	0.000003	-0.0000009	0.0000001	0.282147	0.000004
JMC475 - undoped	11.9	0.02	0.000	0.000001	-0.000016	0.000003	0.0000000	0.0000001	0.282137	0.000004
JMC475 - undoped	11.8	0.02	0.000	0.000001	0.000003	0.000003	0.0000001	0.0000001	0.282138	0.000003
JMC475 - undoped	11.8	0.02	0.000	0.000001	-0.000008	0.000003	-0.0000002	0.0000001	0.282140	0.000004
JMC475 - undoped	12.0	0.02	0.000	0.000001	0.000005	0.000003	0.0000002	0.0000001	0.282134	0.000003
JMC475 - undoped	12.1	0.02	0.000	0.000001	0.000009	0.000003	-0.0000003	0.0000001	0.282128	0.000004
JMC475 - undoped	11.9	0.02	0.000	0.000001	0.000013	0.000003	0.0000006	0.0000001	0.282123	0.000004
JMC475 - undoped	12.1	0.02	0.000	0.000001	0.000031	0.000003	0.0000005	0.0000001	0.282129	0.000004
JMC475 - undoped	12.0	0.02	0.000	0.000001	0.000018	0.000003	0.0000003	0.0000001	0.282128	0.000003
JMC475 - undoped	9.9	0.02	0.000	0.000001	0.000015	0.000004	0.0000002	0.0000001	0.282128	0.000004
JMC475 - undoped	9.8	0.01	0.000	0.000001	0.000002	0.000003	-0.0000001	0.0000001	0.282133	0.000003
JMC475 - undoped	9.7	0.02	0.000	0.000002	0.000013	0.000005	-0.0000003	0.0000001	0.282129	0.000003
average (n=13)	11.5		0.000		0.000003		0.0000000		0.282134	
2SD	1.9		0.000		0.000032		0.0000007		0.000014	
JMC475 - doped	11.9	0.02	0.271	0.000108	0.683869	0.000287	0.0055566	0.0000008	0.282149	0.000005
JMC475 - doped	11.7	0.02	0.270	0.000135	0.681534	0.000354	0.0055502	0.0000007	0.282151	0.000005
JMC475 - doped	9.9	0.01	0.251	0.000062	0.633844	0.000184	0.0053795	0.0000005	0.282143	0.000006
JMC475 - doped	9.8	0.01	0.251	0.000071	0.633122	0.000191	0.0053777	0.0000004	0.282131	0.000004
average (n=4)	10.8		0.260		0.658093		0.0054660		0.282143	
2SD	2.2		0.022		0.056868		0.0002019		0.000018	
<b>14/12/06</b>										
JMC475 - undoped	9.4	0.02	0.000	0.000001	0.000009	0.000004	0.0000000	0.0000001	0.282156	0.000004
JMC475 - undoped	9.3	0.02	0.000	0.000001	0.000008	0.000004	-0.0000005	0.0000002	0.282158	0.000005
JMC475 - undoped	9.2	0.02	0.000	0.000002	0.000002	0.000004	-0.0000002	0.0000001	0.282148	0.000005
JMC475 - undoped	9.3	0.01	0.000	0.000002	0.000008	0.000004	-0.0000005	0.0000001	0.282148	0.000006
JMC475 - undoped	9.3	0.01	0.000	0.000001	0.000016	0.000003	-0.0000002	0.0000001	0.282141	0.000004
JMC475 - undoped	9.2	0.02	0.000	0.000002	0.000006	0.000004	-0.0000001	0.0000001	0.282158	0.000004
JMC475 - undoped	9.2	0.02	0.000	0.000002	-0.000003	0.000005	0.0000002	0.0000002	0.282151	0.000005
JMC475 - undoped	9.2	0.01	0.000	0.000002	0.000007	0.000004	-0.0000005	0.0000001	0.282140	0.000004
JMC475 - undoped	9.2	0.01	0.000	0.000001	0.000004	0.000003	0.0000007	0.0000001	0.282153	0.000004
JMC475 - undoped	9.1	0.01	0.000	0.000001	0.000008	0.000003	-0.0000001	0.0000001	0.282151	0.000005
JMC475 - undoped	8.5	0.01	0.000	0.000002	0.000011	0.000004	0.0000001	0.0000002	0.282148	0.000005
JMC475 - undoped	8.4	0.01	0.000	0.000002	-0.000003	0.000004	0.0000002	0.0000002	0.282141	0.000005
JMC475 - undoped	8.4	0.02	0.000	0.000001	0.000012	0.000004	-0.0000001	0.0000002	0.282150	0.000005
JMC475 - undoped	8.5	0.01	0.000	0.000002	0.000025	0.000004	0.0000009	0.0000002	0.282132	0.000004
JMC475 - undoped	8.9	0.01	0.000	0.000002	0.000005	0.000004	-0.0000001	0.0000001	0.282148	0.000004
JMC475 - undoped	9.1	0.02	0.000	0.000001	-0.000005	0.000003	0.0000009	0.0000001	0.282164	0.000005
average (n=16)	9.0		0.000		0.000007		0.0000000		0.282149	
2SD	0.7		0.000		0.000015		0.0000009		0.000016	
JMC475 - doped	9.2	0.01	0.237	0.000051	0.599317	0.000140	0.0053919	0.0000004	0.282135	0.000005
JMC475 - doped	9.2	0.01	0.238	0.000043	0.600950	0.000119	0.0053919	0.0000004	0.282150	0.000005
JMC475 - doped	9.2	0.01	0.237	0.000041	0.599273	0.000121	0.0053861	0.0000004	0.282143	0.000005
JMC475 - doped	9.2	0.01	0.237	0.000058	0.598782	0.000155	0.0053840	0.0000004	0.282167	0.000005
JMC475 - doped	9.1	0.01	0.237	0.000049	0.598935	0.000142	0.0053858	0.0000004	0.282162	0.000004
JMC475 - doped	9.2	0.01	0.236	0.000047	0.597413	0.000123	0.0053779	0.0000004	0.282149	0.000006
JMC475 - doped	8.7	0.01	0.232	0.000038	0.587203	0.000106	0.0053348	0.0000003	0.282156	0.000006
JMC475 - doped	8.6	0.01	0.233	0.000034	0.587649	0.000100	0.0053372	0.0000003	0.282154	0.000005
average (n=8)	9.1		0.236		0.596190		0.0053737		0.282152	
2SD	0.5		0.004		0.010991		0.0000474		0.000021	
<b>15/12/06</b>										
JMC475 - undoped	8.9	0.02	0.000	0.000001	0.000006	0.000004	0.0000000	0.0000001	0.282148	0.000004
JMC475 - undoped	8.9	0.02	0.000	0.000002	0.000007	0.000004	-0.0000004	0.0000002	0.282148	0.000004
JMC475 - undoped	8.9	0.02	0.000	0.000001	-0.000009	0.000003	0.0000001	0.0000001	0.282154	0.000004
average (n=3)	8.9		0.000		0.000002		-0.0000001		0.282150	
2SD	0.0		0.000		0.000018		0.0000004		0.000007	
JMC475 - doped	9.2	0.03	0.241	0.000099	0.610867	0.000264	0.0054659	0.0000007	0.282148	0.000005
JMC475 - doped	9.3	0.02	0.241	0.000069	0.610453	0.000190	0.0054602	0.0000007	0.282146	0.000004
average (n=2)	9.2		0.241		0.610660		0.0054631		0.282147	
2SD	0.1		0.000		0.000585		0.0000081		0.000003	
<b>07/02/07</b>										
JMC475 - undoped	8.1	0.01	0.000	0.000001	-0.000006	0.000004	0.0000003	0.0000002	0.282163	0.000006
JMC475 - undoped	8.0	0.01	0.000	0.000002	0.000013	0.000005	0.0000004	0.0000001	0.282165	0.000004
JMC475 - undoped	8.2	0.01	0.000	0.000001	-0.000006	0.000004	-0.0000002	0.0000002	0.282170	0.000004
JMC475 - undoped	8.1	0.03	0.000	0.000002	0.000006	0.000004	0.0000002	0.0000001	0.282152	0.000004

	total Hf	1 $\sigma$	Yb/Hf	1 $\sigma$	<sup>176</sup> Yb/ <sup>177</sup> Hf	1 $\sigma$	<sup>176</sup> Lu/ <sup>177</sup> Hf	1 $\sigma$	<sup>176</sup> Hf/ <sup>177</sup> Hf	1 $\sigma$
JMC475 - undoped	7.8	0.01	0.000	0.000002	-0.000002	0.000005	0.0000008	0.0000002	0.282160	0.000005
JMC475 - undoped	7.7	0.01	0.000	0.000002	0.000002	0.000004	0.0000006	0.0000002	0.282166	0.000004
JMC475 - undoped	8.0	0.02	0.000	0.000002	0.000024	0.000005	0.0000000	0.0000002	0.282160	0.000005
average (n=7)	8.0		0.000		0.000004		0.0000003		0.282162	
2SD	0.4		0.000		0.000021		0.0000007		0.000012	
JMC475 - doped	9.5	0.02	0.262	0.000162	0.664747	0.000430	0.0050835	0.0000016	0.282152	0.000004
JMC475 - doped	9.7	0.02	0.262	0.000115	0.662352	0.000289	0.0050752	0.0000007	0.282177	0.000005
JMC475 - doped	9.1	0.01	0.259	0.000089	0.655427	0.000236	0.0050364	0.0000005	0.282190	0.000004
JMC475 - doped	9.3	0.02	0.258	0.000087	0.653079	0.000247	0.0050311	0.0000006	0.282168	0.000006
average (n=4)	9.4		0.260		0.658901		0.0050565		0.282172	
2SD	0.5		0.004		0.011079		0.0000532		0.000031	
<u>08/02/07</u>										
JMC475 - undoped	9.4	0.02	0.000	0.000002	-0.000003	0.000004	-0.0000010	0.0000001	0.282148	0.000004
JMC475 - undoped	9.3	0.02	0.000	0.000002	0.000000	0.000004	-0.0000004	0.0000001	0.282157	0.000004
JMC475 - undoped	8.9	0.02	0.000	0.000001	0.000013	0.000004	0.0000013	0.0000001	0.282156	0.000004
JMC475 - undoped	9.2	0.02	0.000	0.000002	-0.000010	0.000004	-0.0000001	0.0000001	0.282161	0.000004
average (n=4)	9.2		0.000		0.000000		-0.0000001		0.282155	
2SD	0.4		0.000		0.000020		0.0000019		0.000011	
JMC475 - doped	11.0	0.02	0.289	0.000176	0.729128	0.000451	0.0051518	0.0000009	0.282160	0.000005
JMC475 - doped	10.4	0.02	0.286	0.000129	0.720559	0.000332	0.0051092	0.0000010	0.282168	0.000005
JMC475 - doped	10.9	0.02	0.288	0.000218	0.725945	0.000567	0.0051252	0.0000009	0.282157	0.000005
JMC475 - doped	10.9	0.02	0.287	0.000173	0.722760	0.000423	0.0051206	0.0000007	0.282169	0.000005
average (n=4)	10.8		0.287		0.724598		0.0051267		0.282163	
2SD	0.6		0.003		0.007486		0.0000360		0.000012	

### Appendix 3d

#### Two-component magma mixing modelling

% Dalradian	$\delta^{18}\text{O}$ [‰]	$\epsilon\text{Hf}_T$	$\epsilon\text{Hf}_C$	% enriched mantle
0	5.5*	1.3*	3.4*	1
0.1	6.4	-0.5	1.4	0.9
0.2	7.2	-2.3	-0.7	0.8
0.3	8.1	-4.2	-2.7	0.7
0.4	9.0	-6.0	-4.7	0.6
0.5	9.9	-7.8	-6.8	0.5
0.6	10.7	-9.6	-8.8	0.4
0.7	11.6	-11.4	-10.8	0.3
0.8	12.5	-13.3	-12.8	0.2
0.9	13.3	-15.1	-14.9	0.1
1	14.2*	-16.9*	-16.9*	0

\*Average enriched mantle and average Dalradian

(data from Anderson et al., 2004; Canning et al., 1998; Eiler, 2001; Frost and O'Nions, 1985; O'Nions et al., 1983; Thirlwall, 1982)

$\epsilon\text{Hf}_T$  = data from Thirlwall (1982)

$\epsilon\text{Hf}_C$  = data from Canning et al. (1998)

## **APPENDIX 4**

### **Supplementary data for Paper 4**



**Appendix 4a**  
**Major, trace and rare earth element whole-rock data**

	<b>Kemnay</b> SA04/07	<b>Cove</b> SA04/10	<b>Nigg Bay</b> SA04/11
SiO <sub>2</sub> [%]	73.4	70.2	71.2
TiO <sub>2</sub>	0.2	0.4	0.3
Al <sub>2</sub> O <sub>3</sub>	14.0	14.8	14.7
Fe <sub>2</sub> O <sub>3</sub>	1.4	2.5	2.6
MnO	0.0	0.0	0.0
MgO	0.1	0.6	0.6
CaO	1.2	1.3	1.6
Na <sub>2</sub> O	3.3	3.0	3.4
K <sub>2</sub> O	4.6	4.3	3.9
P <sub>2</sub> O <sub>5</sub>	0.0	0.1	0.1
LOI	0.7	1.2	1.0
Sum	99.0	98.4	99.3
Sc [ppm]	3	3	5
V		10	20
Cr			9
Ni			
Ba	1126	989	774
Rb	111	117	107
Sr	344	297	219
Y*	6	12	13
U*	3	2	3
Th*	12	14	14
Pb	36	17	25
Zr	108	203	194
Nb	9	16	17
Cu	5	5	10
Zn	40	41	37
La	35.08	56.71	48.77
Ce	67.0	108.2	96.9
Pr	7.17	12.41	10.93
Nd	25.7	45.7	40.0
Sm	4.07	7.63	7.04
Eu	0.95	1.37	1.19
Tb	0.34	0.64	0.65
Gd	2.55	5.37	4.96
Dy	1.46	3.02	3.30
Ho	0.25	0.46	0.49
Er	0.70	1.08	1.22
Tm	0.09	0.14	0.15
Yb	0.58	0.84	0.82
Lu	0.09	0.11	0.11
Hf	3.1	5.2	5.3
R1	3389	3239	3308
R2	357	396	418
A/CNK	1.12	1.23	1.16
A/NK	1.35	1.54	1.50
grid reference	NJ 73788 16821	NJ 95259 00268	NJ 96940 05083

\* trace elements analysed by ICP-MS

## **Appendix 4b: Analytical protocols**

### **1. Whole-rock analyses**

REEs and some trace elements were analysed at the British Geological Survey (BGS) in Nottingham. The samples were fused with  $\text{Na}_2\text{O}_2$  and then leached with deionised water and HCl before analysis using a ThermoElemental PQ Excel quadrupole ICP-MS. Matrix-matched calibration standards were used throughout.

### **2. Zircon sample preparation**

Zircon separation was carried out in the University of St. Andrews Mineral Separation Facility. Rock samples of approximately 5 kg were crushed and sieved to obtain the  $< 500 \mu\text{m}$  fraction from which zircon crystals were separated using a Wilfley Table, heavy liquids and a Frantz magnetic separator. Approximately 100 zircon crystals were hand-picked from the remaining heavy, non-magnetic fraction, providing a range of grain size, morphology, transparency, alteration and occurrence of inclusions or cracks. The crystals were mounted into epoxy (Araldite) and the zircon mounts polished to about half thickness to expose the crystal interiors. The polished surfaces were imaged in back-scattered electron (BSE) and cathodoluminescence (CL) mode using a Philips XL30CP Scanning Electron Microscope (SEM) at the University of Edinburgh to identify internal zoning features, inherited material, inclusions and cracks. Suitable crystals for in-situ oxygen isotope analysis were selected using this information.

### **3. Zircon oxygen isotope analysis**

Zircon oxygen isotope data were obtained using a Cameca ims-1270 ion microprobe at the University of Edinburgh following the methods of Cavosie et al. (2005) and Kemp et al. (2006). A 6nA primary  $^{133}\text{Cs}^+$  ion beam with a diameter of c.  $20 \mu\text{m}$  was used, charge was neutralised using a normal-incidence electron flood gun, secondary ions were extracted at 10 kV, and  $^{18}\text{O}^-$  and  $^{16}\text{O}^-$  ions were monitored simultaneously on dual Faraday cups. Secondary ion beam centring, pre-sputtering for 50 seconds and subsequent data collection over 10 cycles (total counting time: 40 seconds = 4 seconds per cycle) resulted in a total acquisition time of c. 200 seconds.

The secondary yield of  $^{18}\text{O}$  under these conditions was typically between  $4.5 \times 10^6$  and  $5.5 \times 10^6$  counts per second. To correct for instrumental mass fractionation (IMF) and instrumental drift, all data were normalised to zircon standard 91500 ( $\delta^{18}\text{O} = 9.86 \text{ ‰}$ ) (Wiedenbeck et al., 2004), which was analysed in blocks of 5 to 10 after every 10 to 15 unknown zircon analyses. During stable instrument conditions the unknown zircon analyses were normalised to the daily average  $^{18}\text{O}/^{16}\text{O}$  value obtained for 91500. In cases where instrumental drift was recognised, the analytical conditions changed or sample exchange was carried out, the data were divided into sessions in which unknowns were normalised to the linearly interpolated  $^{18}\text{O}/^{16}\text{O}$  value derived from analyses of the bracketing 91500 standard.

Prior to oxygen isotope analysis,  $\text{HfO}_2$  concentrations in the zircons were measured by electron microprobe as variations in  $\text{HfO}_2$  have been shown to cause variations in IMF (Peck et al., 2001). This has been shown to be particularly important when conducting analysis using e.g. a Cameca ims-4f at high-energy offset. However, in this study oxygen isotope analysis were carried out using a Cameca ims-1270 ion microprobe, and in both diorite samples  $\text{HfO}_2$  variations in zircons were  $\leq 0.5 \text{ wt } \%$ ; therefore corrections for IMF were unnecessary. The internal precision of the analyses based on counting statistics varied between 0.1-0.4 ‰ (1SD). External precision based on the reproducibility of standard 91500 ranged from 0.2-0.7 ‰ (2SD) and 0.031-0.145 (1 s.e.m.).

Analyses were conducted in clear, crack- and inclusion-free areas of representative zircon crystals. Where possible, multiple analyses (core to rim) were carried out on single zircon crystals to document zircon growth histories, and occasionally also in adjacent spots within crystals to assess reproducibility. The ion probe pits were subsequently imaged in BSE and SE mode using an SEM to determine the exact position of the analyses and to ensure that no cracks in the bottom of the pit might have influenced the results. Data obtained from suspect locations were rejected. In addition, data were excluded when the correction on the position of the secondary ion beam was anomalously large.

#### 4. U-Th-Pb analysis

Subsequent to oxygen isotope analysis, U-Th-Pb analyses were carried out also using the Cameca ims-1270 at the EIMF. Analytical procedures are similar to those described by Schuhmacher et al. (1994) and Whitehouse et al. (1997), and are described in detail in Kelly et al. (accepted). Zircons were analysed using a  $\sim 4\text{nA O}_2^-$  primary ion source with 22.5 keV net impact energy. The beam was focused using Köhler illumination, with primary beam alignment giving ellipsoidal analysis pits ( $\sim 25\text{ }\mu\text{m}$  max. dimension). Spatial resolution of the analysed area was further limited by the use of the field aperture. U, Th and Pb were analysed at a mass resolution ( $M/\Delta M$ ) of  $\sim 4000R$  using a peak switching routine. An energy window of 60 eV was used throughout, with energy centring on each analysis using the HfO peak. Oxygen flooding on the surface of the sample was employed to enhance Pb ion yields. Prior to analysis the sample surface was pre-rastered over an area of  $\sim 40\text{ }\mu\text{m}$  for 120 seconds to remove any surface contamination.

Calibration of Pb/U ratios followed procedures employed by other SHRIMP and/or Cameca ims-1270 laboratories and were based on the observed relationship between Pb/U and ratios of UO/U (e.g. Claoué-Long et al., 1995; Compston et al., 1984; Schuhmacher et al., 1994; Williams, 1998; Williams and Claesson, 1987; Whitehouse et al., 1997). However, the relationship  $\ln(\text{Pb}/\text{U})$  vs.  $\ln(\text{UO}_2/\text{UO})$  was found to give a better within-session reproducibility than the conventional  $\ln(\text{Pb}/\text{U})$  vs.  $\ln(\text{UO}/\text{U})$  or  $\ln(\text{Pb}/\text{U})$  vs.  $\ln(\text{UO}_2/\text{U})$  methods.

U/Pb ratios were calibrated against measurements on standard 91500 (Wiedenbeck et al., 1995:  $\sim 1062.5\text{ Ma}$ ; assumed  $^{206}\text{Pb}/^{238}\text{U}$  ratio = 0.17917), which is measured after 3-4 unknowns. Temora 2 was analysed as a secondary standard after every 10-15 analyses. Th/U ratios in unknowns were calculated by reference to measurements of Th/U and  $^{208}\text{Pb}/^{206}\text{Pb}$  on the 91500 standard ( $\text{Th}/\text{U} = 0.362$ ), assuming closed system behaviour. Elemental concentrations were determined based on the observed oxide ratios of the standard ( $\text{UO}_2/\text{Zr}_2\text{O}_2$  and  $\text{HfO}/\text{Zr}_2\text{O}_2$ ; assuming  $\text{U} = 81.2\text{ ppm}$ ,  $\text{Hf} = 5880\text{ ppm}$ ).

Corrections were carried out for dead time, detector background ( $\sim 0.025$  counts/second) and common Pb. Common Pb corrections were made using the measured  $^{204}\text{Pb}$  counts above detector background and the modern day composition

of common Pb. Typically  $^{204}\text{Pb}$  count rates approached the background, which led to corrections of < 15 ppb on  $^{206}\text{Pb}$ .

Uncertainties on the Pb/U ratios include an error based on observed uncertainty from each measured ratio, which is generally close to that expected from counting statistics. Observed uncertainties on the U/Pb ratio of 91500 are generally an additional 0.3% in excess of that expected from counting statistics alone. This is assumed to be a random error (see also Ireland and Williams, 2003) and has been propagated (in both standards and unknowns) together with the observed variation in Pb/U ratios measured for each analysis (typically close to the counting errors). For measurement of the 91500 standard, uncertainties are typically between 0.7-1.0 % per analysis. Uncertainties on  $^{207}\text{Pb}/^{206}\text{Pb}$  ratios are based on observed variations from cycle to cycle during each analysis and commonly approach those expected from counting statistics. Uncertainties on ages quoted in the text and in tables for *individual analyses* (ratios and ages) are at the  $1\sigma$  level. All uncertainties in calculated *group* ages are reported at  $2\sigma$  level or 95 % confidence.

Plots and age calculations have been made using the computer program ISOPLOT/EX v3 (Ludwig, 2003). Ages of magmatic grains are presented as weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  average ages and include only concordant data points; ages of inherited grains (> 1000 Ma) are  $^{207}\text{Pb}/^{206}\text{Pb}$  ages. Following analysis, the ion probe pits were imaged in BSE and SE mode to check for inclusions and cracks in the bottom of the pit. Data obtained from dubious locations were rejected. During data processing we noticed that zircons with high U concentrations (>1000 ppm) commonly give older ages or lie off Concordia. Electron back-scatter diffractometry (EBSD) of these zircons showed disturbance and even complete destruction of their crystal structure. To provide a robust data set we excluded all data obtained from zircons showing above 1000 ppm U. In addition, zircons displaying high common Pb concentrations and/or > 10 % discordance were also rejected (summarised data are presented in Table 1; full data sets in Appendix 3).

## 5. Hf isotope analysis

Hafnium isotope analysis was carried out at the NERC Isotope Geosciences Laboratory (NIGL) in Nottingham, using a Nu Instruments Nu-Plasma HR multi-

collector ICP-MS coupled to a New Wave Research UP193SS 193nm solid state laser ablation system. For an improved wash-out a low volume ablation cell (NIGL zircon cell) was employed. Ablation was conducted in a He atmosphere (0.8-1.0 l/min). Ar make-up gas was sourced from a Nu Instruments DSN-100 desolvating nebuliser whilst aspirating 2 % HNO<sub>3</sub> and 0.1 molar HF to maintain constant plasma conditions.

At the time of analysis the mass spectrometer was fitted with a specially designed U-Pb collector block, which limits the number of Faraday cups available for Hf isotope analysis to seven. The instrument is therefore restricted to measuring <sup>173</sup>Yb, <sup>174</sup>Lu, <sup>175</sup>Lu, <sup>176</sup>(Yb, Lu, Hf), <sup>177</sup>Hf, <sup>178</sup>Hf and <sup>179</sup>Hf. The stable isotopes <sup>180</sup>Hf and <sup>181</sup>Hf are not analysed and emphasis is placed on the <sup>178</sup>Hf/<sup>177</sup>Hf stable isotope ratio for monitoring of data quality. A peak jumping routine including <sup>172</sup>Yb, to allow assessment of the effect of using a Yb mass bias correction for the Yb interference correction rather than the Hf mass bias correction, has been investigated but was found unnecessary with the data for both being equivalent within the increased uncertainty reflected by the low Yb concentrations.

The isobaric interference correction for <sup>176</sup>Yb was determined prior to each analytical session using Yb doped JMC475 Hf standards. This correction was determined for total Yb/Hf ratios of up to 0.3. These data were used to calculate a true ratio for the <sup>176</sup>Yb/<sup>173</sup>Yb of 0.79488. The Lu interference correction used the accepted ratio of <sup>176</sup>Lu/<sup>175</sup>Lu = 0.02653. During measurement the <sup>173</sup>Yb and <sup>175</sup>Lu peaks were monitored and corrections applied according to these ratios. Each day spiked and unspiked solution standards were analysed to monitor instrument performance and effectiveness of the corrections.

Ablation data were acquired using a static spot ablation protocol, a 50 µm beam and a 5-10 Hz laser pulse repetition rate. A fluence of 4-6 J/cm<sup>2</sup> and ablation time of 70 seconds resulted in an ablation rate of 0.05-0.09 µm/pulse (0.5-0.9 µm/sec). Total Hf signals varied between 4.5-6.5 V resulting in reproducibilities of the Mud Tank reference material between 0.7 and 1.0 εHf units (2σ). The Mud Tank zircon reference material was used to normalise the sample zircons and assess the reproducibility of all ratios. This included normalisation of the Lu-Hf ratio required for age correction. All values for Mud Tank were taken from Woodhead and Hergt

(2005). All uncertainty components, including those for age and normalisation, were factored into the expanded uncertainty quoted.

For Hf isotope analysis zircons were selected for which U-Pb and (in most cases) oxygen isotope data already existed in order to enable correlation of the different data sets. Where possible multiple analyses were made on a single crystal. However, due to the much larger spot size of the laser in comparison to the ion probe this was seldom possible. Most data were obtained from crystal cores, which were easier to analyse as they often define the largest part of the crystal, and only rarely of the rim. Cracks and inclusions were always avoided and all analyses were carried out on the already existing SIMS spots or at least within the same CL growth zone. The ablation data were normalised to Mud Tank ( $^{176}\text{Hf}/^{177}\text{Hf}_{\text{solution}} = 0.282507 \pm 6$  and  $^{176}\text{Lu}/^{177}\text{Hf}_{\text{solution}} = 0.000042$  (Woodhead and Hergt, 2005)). Reproducibility of the Mud Tank standard was propagated into the uncertainty of the sample analysis.

In the rare cases where the laser drilled through the zircon grains or from an older inherited core into the surrounding magmatic rim, the analyses were examined using NIGL's time-resolved software, which allowed identification of the most stable parts of the profile and of distinguishable Hf isotope zones.

$\varepsilon\text{Hf}$  values were calculated using a  $^{176}\text{Lu}$  decay constant of  $1.865 \times 10^{-11}\text{y}^{-1}$  (Scherer et al., 2001), the present-day chondritic  $^{176}\text{Lu}/^{177}\text{Hf}$  value of 0.0332 and  $^{176}\text{Hf}/^{177}\text{Hf}$  ratio of 0.282772 (Blichert-Toft and Albarède, 1997). To calculate two-stage Hf model ages the  $^{176}\text{Lu}/^{177}\text{Hf}$  ratios of the average crust ( $\text{TDM}_\text{C}$ ) ( $^{176}\text{Lu}/^{177}\text{Hf} = 0.015$  (Griffin et al., 2002)) and of the depleted mantle ( $^{176}\text{Lu}/^{177}\text{Hf} = 0.0384$  (Griffin et al., 2000)), the initial  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios of the zircon and the depleted mantle (present-day  $^{176}\text{Hf}/^{177}\text{Hf}$  ratio of the depleted mantle = 0.28325 (Nowell et al., 1998)), and the U-Pb SIMS age were used. For comparison, two-stage Hf model ages were also calculated based on the whole-rock  $^{176}\text{Lu}/^{177}\text{Hf}$  ratio of each sample ( $\text{TDM}_\text{W}$ ) (summarised data in Table 1; full data set in Appendix 5).

## Zircon U-Pb data of the Kernav. Cove and Nigq Bay granites

rejected, > 10 % discordant  
rejected, > 10 % discordant  
rejected, high common Pb



sample	analysis no.	grain U no. ppm	Th ppm	Pb ppm	Th/U ppb	<sup>204</sup> Pb/ ppb	t206 (%)	<sup>206</sup> Pb/ <sup>238</sup> Pb	corrected ratios				Ages (Ma)				grain area	comment			
									<sup>207</sup> Pb/ <sup>235</sup> U	1σ	<sup>206</sup> Pb/ <sup>238</sup> Pb	1σ	<sup>207</sup> Pb/ <sup>235</sup> U	1σ	<sup>206</sup> Pb/ <sup>238</sup> Pb	1σ					
SA04/10 - 9.17		9	1430	52	95	0.63	1.5	0.38	0.0002019	0.0722	0.0011	0.1854	0.0037	1.6786	0.0301	0.1686	0.0016	0.52	inh	inherited core	
SA04/10 - 9.18		9	540	51	95	0.04	18.4	0.39	0.000268	0.0556	0.0003	0.0108	0.0013	0.5508	0.0032	0.0719	0.0006	0.85	inh	rejected, high common Pb	
SA04/10 - 7.13		7	1908	74	136	0.04	33.3	0.49	0.000260	0.0556	0.0007	0.0095	0.0014	0.5905	0.0089	0.0771	0.0006	0.53	inh	rejected, high common Pb	
SA04/10 - 7.14		7	146	9	10	0.06	1.1	0.22	0.0001168	0.0551	0.0008	0.0163	0.0020	0.5500	0.0095	0.0724	0.0006	0.49	inh	rejected, high common Pb	
SA04/10 - 12.22		12	44	21	5	0.50	146.7	38.34	0.0332459	0.0536	0.0014	0.1518	0.0201	0.5697	0.0283	0.1164	0.0025	0.64	inh	rejected, high common Pb	
SA04/10 - 12.24		12	235	68	17	0.29	1.2	0.16	0.0000831	0.0558	0.0006	0.0901	0.0017	0.5821	0.0078	0.0731	0.0006	0.59	inh	inherited core, > 10 % discordant	
SA04/10 - 20.46		20	25	14	8	0.96	0.4	0.10	0.0000540	0.1346	0.0031	0.2215	0.0110	5.5165	0.1623	0.2972	0.0023	0.74	inh	inherited core, > 10 % discordant	
SA04/10 - 20.47		20	317	70	69	0.23	0.6	0.02	0.0000096	0.1051	0.0013	0.0628	0.0008	3.1271	0.0711	0.2157	0.0029	0.74	inh	rejected, > 10 % discordant	
SA04/10 - 19.43		19	139	62	10	0.46	532.8	60.31	0.0812751	0.0264	0.0004	0.0203	0.0023	0.2217	0.0043	0.0609	0.0008	0.27	inh	rejected, crack	
SA04/10 - 19.45		19	45	29	4	0.66	1.3	0.85	0.0004598	0.0618	0.0020	0.1901	0.0023	0.5084	0.0203	0.0714	0.0008	0.27	inh	rejected, > 10 % discordant	
SA04/10 - 16.33		16	299	179	81	0.61	13.8	0.40	0.0002138	0.1093	0.0005	0.1959	0.0023	3.7212	0.0358	0.2468	0.0021	0.88	c2a	rejected, crack	
SA04/10 - 16.34		16	815	30	56	0.04	18.1	0.65	0.0003481	0.0577	0.0015	0.2065	0.0072	0.5788	0.0064	0.0736	0.0006	0.73	inh	rejected, crack	
SA04/10 - 14.28		14	74	50	6	0.89	1.9	0.79	0.0004275	0.0671	0.0008	0.1800	0.0025	0.5966	0.0155	0.0715	0.0006	0.36	c1	rejected, > 10 % discordant	
SA04/10 - 14.28B		14	105	59	8	0.58	0.6	0.16	0.0000863	0.0553	0.0012	0.0684	0.0072	0.5267	0.0097	0.0724	0.0007	0.57	c2	rejected, > 10 % discordant	
SA04/10 - 14.30		14	220	54	16	0.25	14.1	1.92	0.0010443	0.0631	0.0012	0.1199	0.0023	0.5567	0.0125	0.0717	0.0006	0.33	inh	rejected, > 10 % discordant	
SA04/10 - 15.31		15	224	84	16	0.38	1.8	0.24	0.0001273	0.0561	0.0006	0.1184	0.0042	0.5594	0.0077	0.0723	0.0007	0.57	c1	rejected, > 10 % discordant	
SA04/10 - 15.32		15	75	41	6	0.56	0.9	0.37	0.0001963	0.0628	0.0015	0.1724	0.0042	0.5324	0.0153	0.0709	0.0008	0.38	c2	rejected, crack	
SA04/10 - 13.25		13	56	20	8	0.37	121.7	26.29	0.0190742	0.0766	0.0002	0.1024	0.0004	1.7125	0.0325	0.1353	0.0018	0.49	inh	inherited core, > 10 % discordant	
SA04/10 - 17.36		17	661	220	120	0.34	1.7	0.03	0.0000170	0.0553	0.0003	0.0035	0.0007	0.5676	0.0058	0.0745	0.0006	0.80	inh	rejected, crack	
SA04/10 - 17.35		17	526	9	36	0.02	2.2	0.12	0.0000654	0.0591	0.0016	0.0283	0.0051	0.5933	0.0169	0.0728	0.0007	0.32	inh	rejected, high common Pb	
SA04/10 - 7.14B		7	124	9	8	0.08	4.7	1.12	0.0006045	0.0591	0.0016	0.0283	0.0051	0.5933	0.0169	0.0728	0.0007	0.32	inh	rejected, high common Pb	
SA04/10 - 20.46B		20	120	42	53	0.36	0.3	0.01	0.000067	0.1658	0.0012	0.1015	0.0008	9.1538	0.1140	0.0405	0.0040	0.81	inh	inherited core, > 10 % discordant	
SA04/10 - 20.47B		20	294	76	51	0.26	13.8	0.59	0.0003176	0.0995	0.0009	0.0736	0.0041	2.3442	0.0539	0.1708	0.0036	0.92	inh	rejected, high common Pb	
SA04/10 - 15.32B		15	133	108	11	0.84	1.0	0.22	0.0001156	0.0557	0.0008	0.2592	0.0027	0.5761	0.0103	0.0751	0.0007	0.52	inh	rejected, high common Pb	
SA04/10 - 17.38B		17	296	70	54	0.24	0.8	0.03	0.0000164	0.0785	0.0013	0.0744	0.0012	1.9763	0.0373	0.1827	0.0017	0.51	c1	rejected, > 10 % discordant	
SA04/10 - 17.38B		17	896	10	63	0.01	129.7	39.3	0.0021888	0.0531	0.0011	0.0000	0.0000	0.5614	0.0125	0.1827	0.0017	0.51	inh	rejected, > 10 % discordant	
SA04/10 - 5.8B		5	99	72	8	0.75	0.6	0.18	0.0000964	0.0566	0.0011	0.2310	0.0032	0.5720	0.0124	0.0749	0.0008	0.47	inh	rejected, > 10 % discordant	
SA05/10 - 5.8C		5	65	52	6	0.82	0.3	0.15	0.0000798	0.0567	0.0011	0.2554	0.0032	0.5857	0.0129	0.0749	0.0008	0.48	c2a	rejected, high common Pb	
SA04/10 - 9.17B		9	42	23	8	0.55	0.6	0.18	0.0000946	0.0747	0.0012	0.1698	0.0027	1.7825	0.0365	0.1731	0.0021	0.58	c2b	rejected, high common Pb	
SA04/10 - 13.25B		13	39	18	6	0.48	137.8	35.15	0.0289898	0.0694	0.0018	0.1208	0.0179	1.3667	0.0411	0.1428	0.0022	0.51	inh	rejected, crack	
SA04/10 - 21.49		21	370	178	100	0.49	2.6	0.06	0.0000322	0.0922	0.0004	0.1457	0.0007	3.2080	0.0302	0.2522	0.0022	0.91	inh	rejected, crack	
SA04/10 - 21.50		21	1419	93	78	0.07	212.8	52.3	0.0029506	0.0616	0.0033	0.0218	0.0038	0.4987	0.0278	0.0587	0.0008	0.25	inh	rejected, > 10 % discordant	
SA05/10 - 22.51		22	190	74	90	0.40	0.9	0.02	0.0000131	0.1836	0.0005	0.1276	0.0014	0.6569	0.1304	0.0421	0.0049	0.94	inh	inherited core, > 10 % discordant	
SA05/10 - 8.15		8	344	143	98	0.43	6.6	0.16	0.0000835	0.1081	0.0005	0.1276	0.0014	3.9733	0.0382	0.2666	0.0023	0.90	inh	rejected, crack	
SA05/10 - 8.16		8	1185	28	81	0.02	146.8	34.8	0.0019275	0.0549	0.0008	0.0063	0.0010	0.5626	0.0091	0.0743	0.0006	0.52	inh	rejected, high common Pb	
SA05/10 - 10.19		10	1154	136	170	0.12	1.6	0.02	0.0000105	0.0715	0.0002	0.0364	0.0003	1.5169	0.0135	0.1539	0.0013	0.94	inh	rejected, U > 1000 ppm	
SA05/10 - 10.20		10	1423	17	98	0.01	17.6	0.35	0.0001896	0.0564	0.0004	0.0028	0.0006	0.5857	0.0065	0.0753	0.0006	0.78	inh	rejected, crack	
SA05/10 - 11.21		11	1005	43	69	0.04	62.5	1.76	0.0009588	0.0567	0.0007	0.0161	0.0025	0.5840	0.0085	0.0747	0.0006	0.60	inh	rejected, crack	
Nigg Bay Granite																					
SA04/11 - 3.5		3	112	29	20	0.26	1.9	0.21	0.0001111	0.0777	0.0008	0.0922	0.0030	1.9097	0.0314	0.1784	0.0023	0.78	inh	inherited core	
SA04/11 - 3.6		3	505	30	77	0.06	7.9	0.21	0.0001138	0.0725	0.0004	0.0120	0.0013	1.6053	0.0227	0.1607	0.0021	0.84	inh	rejected, high common Pb	
SA04/11 - 10.22		10	76	34	44	0.46	1.2	0.07	0.0000350	0.1986	0.0013	0.1288	0.0014	13.6930	0.2087	0.5003	0.0062	0.81	inh	rejected, crack	
SA04/11 - 10.21		10	660	64	121	0.10	29.7	0.52	0.0002789	0.0992	0.0004	0.0254	0.0019	2.5612	0.0248	0.1873	0.0017	0.92	inh	rejected, high common Pb	
SA04/11 - 14.32		14	1048	61	78	0.06	6.6	0.17	0.0000919	0.0562	0.0003	0.0179	0.0011	0.6172	0.0060	0.0796	0.0006	0.82	inh	rejected, crack	
SA04/11 - 14.34		14	111	22	13	0.15	0.0000800	0.0844	0.0011	0.0819	0.0022	0.0925	0.0025	1.8825	0.0601	0.1617	0.0047	0.92	inh	rejected, crack	
SA04/11 - 26.68a		26	95	77	19	0.82	0.5	0.08	0.0000405	0.0758	0.0009	0.3796	0.0034	1.9367	0.0375	0.1757	0.0029	0.80	inh	rejected, crack	
SA04/11 - 26.68b		26	95	77	19	0.82	0.5	0.08	0.0000405	0.0772	0.0010	0.2403	0.0074	1.9654	0.0487	0.1753	0.0029	0.81	inh	rejected, crack	
SA04/11 - 26.67		26	497	22	34	0.04	25.2	1.47	0.0008003	0.0577	0.0010	0.1016	0.0006	0.5853	0.0136	0.0735	0.0012	0.67	inh	rejected, high common Pb	
SA04/11 - 26.73		26	568	4	39	0.01	19.1	0.10	0.0000515	0.0555	0.0004	0.0099	0.0009	1.6662	0.0093	0.0740	0.0007	0.78	inh	rejected, high common Pb	
SA04/11 - 36.97		36	11	32	3	2.99	0.9	0.66	0.0003558	0.0723	0.0028	0.1597	0.0081	1.7222	0.0732	0.1729	0.0028	0.38	inh	rejected, high common Pb	
SA04/11 - 36.98		36	404	5	28	0.01	9.7	0.26	0.0001419	0.0806	0.0043	0.0151	0.0125	1.6313	0.0073	0.1096	0.0048	0.26	inh	rejected, crack	
SA04/11 - 35.86		35	798	128	139	0.16	7.2	0.11	0.0000592	0.0565	0.0004	0.0497	0.0011	1.9306	0.0275	0.1768	0.0024	0.95	inh	rejected, crack	
SA04/11 - 35.87		33	655																		



sample	analysis no.	grain U ppm	Th ppm	Pb ppm	Th/U ppb	<sup>204</sup> Pb/ ppb	1206 (%)	<sup>206</sup> Pb/ ppb	corrected ratios				Alges (Ma)				comment	
									<sup>207</sup> Pb/ 1σ	<sup>206</sup> Pb/ 1σ	<sup>207</sup> Pb/ 1σ	<sup>206</sup> Pb/ 1σ	<sup>207</sup> Pb/ 1σ	<sup>206</sup> Pb/ 1σ	<sup>207</sup> Pb/ 1σ	<sup>206</sup> Pb/ 1σ		
91500		167	80.1	27.5	15.0	0.35	0.4	0.05	0.0000283	0.0735	0.0007	0.1059	0.0013	1.8569	0.0256	1.832	0.0018	0.72
91500		172	80.9	28.0	14.9	0.36	0.0	0.00	0.0000001	0.0749	0.0011	0.1053	0.0009	1.8544	0.0338	1.795	0.0018	0.56
91500		176	80.0	27.6	14.6	0.35	0.0	0.00	0.0000001	0.0743	0.0008	0.1061	0.0011	1.8304	0.0281	1.767	0.0020	0.79
91500		181	83.1	29.1	15.3	0.36	0.5	0.07	0.0000362	0.0758	0.0008	0.1070	0.0015	1.8765	0.0282	1.795	0.0018	0.67
91500		185	83.3	29.0	15.2	0.36	0.6	0.09	0.0000475	0.0733	0.0008	0.1070	0.0015	1.8039	0.0277	1.766	0.0018	0.67
91500		190	83.8	29.2	15.6	0.36	0.0	0.00	0.0000001	0.0748	0.0006	0.1063	0.0010	1.8725	0.0248	1.816	0.0019	0.79
91500		194	81.6	28.2	15.0	0.35	0.2	0.03	0.0000168	0.0759	0.0007	0.1070	0.0009	1.8737	0.0244	1.797	0.0017	0.71
91500		199	82.4	28.4	15.2	0.35	0.4	0.05	0.0000283	0.0743	0.0008	0.1068	0.0012	1.8441	0.0260	1.800	0.0017	0.69
91500		203	80.0	27.7	14.6	0.36	0.0	0.06	0.0000300	0.0750	0.0009	0.1068	0.0013	1.8492	0.0284	1.789	0.0018	0.64
91500		208	79.6	27.5	14.3	0.36	0.0	0.00	0.0000001	0.0747	0.0008	0.1071	0.0010	1.8105	0.0269	1.759	0.0017	0.65
91500		212	76.3	26.2	14.0	0.35	0.4	0.06	0.0000319	0.0754	0.0007	0.1070	0.0012	1.8625	0.0254	1.793	0.0017	0.69
91500		217	80.3	27.8	14.8	0.36	0.6	0.09	0.0000463	0.0736	0.0009	0.1052	0.0011	1.8226	0.0300	1.795	0.0019	0.64
91500		221	77.6	26.7	13.8	0.35	0.0	0.00	0.0000001	0.0746	0.0010	0.1083	0.0011	1.7915	0.0302	1.742	0.0019	0.65
91500		226	80.6	28.1	14.5	0.36	0.0	0.00	0.0000001	0.0741	0.0009	0.1073	0.0010	1.8001	0.0290	1.763	0.0018	0.62
91500		230	82.2	28.6	14.8	0.36	0.0	0.00	0.0000001	0.0740	0.0009	0.1081	0.0009	1.7955	0.0283	1.759	0.0017	0.62
91500		234	82.0	28.6	15.0	0.36	0.3	0.04	0.0000207	0.0747	0.0007	0.1082	0.0012	1.8439	0.0259	1.789	0.0019	0.74
91500		0	79.0	27.7	14.4	0.36	0.2	0.03	0.0000147	0.0749	0.0006	0.1087	0.0009	1.8427	0.0259	1.783	0.0020	0.80
91500		239	81.3	28.5	14.9	0.36	0.7	0.10	0.0000536	0.0766	0.0008	0.1061	0.0016	1.8813	0.0284	1.782	0.0020	0.73
91500		240	81.5	28.5	14.9	0.36	0.0	0.00	0.0000001	0.0741	0.0008	0.1087	0.0010	1.8234	0.0283	1.784	0.0019	0.70
91500		243	83.0	29.1	15.5	0.36	0.0	0.00	0.0000001	0.0757	0.0007	0.1084	0.0011	1.8966	0.0288	1.817	0.0021	0.76
temora		10	624.0	334.6	44.3	0.55	1.9	0.10	0.0000537	0.0548	0.0004	0.1713	0.0011	0.5049	0.0058	0.069	0.0006	0.73
temora		19	630.4	319.0	44.1	0.52	0.4	0.02	0.0000119	0.0553	0.0004	0.1607	0.0008	0.5055	0.0053	0.064	0.0006	0.79
temora		29	163.6	39.2	10.8	0.25	1.0	0.19	0.0000102	0.0540	0.0007	0.0740	0.0021	0.5036	0.0082	0.0676	0.0006	0.55
temora		38	149.6	45.7	10.0	0.31	0.1	0.03	0.0000152	0.0553	0.0007	0.0975	0.0008	0.5104	0.0078	0.0669	0.0006	0.61
temora		47	198.8	57.9	13.2	0.30	0.8	0.13	0.0000713	0.0555	0.0006	0.0916	0.0017	0.5103	0.0074	0.0667	0.0006	0.59
temora		60	161.6	41.2	10.3	0.26	0.6	0.12	0.0000651	0.0550	0.0007	0.0787	0.0017	0.4908	0.0073	0.0648	0.0006	0.59
temora		69	223.9	64.2	14.6	0.29	0.0	0.00	0.0000001	0.0555	0.0006	0.0921	0.0007	0.5022	0.0070	0.0656	0.0006	0.65
temora		78	176.2	49.1	11.2	0.29	0.2	0.03	0.0000154	0.0554	0.0007	0.0882	0.0010	0.4914	0.0079	0.0644	0.0006	0.65
temora		87	178.4	45.4	11.5	0.26	0.0	0.00	0.0000001	0.0548	0.0007	0.0821	0.0007	0.4937	0.0074	0.0653	0.0006	0.60
temora		TEM 187.8	65.8	12.5	0.36	0.4	0.07	0.0000400	0.0561	0.0005	0.1098	0.0015	0.5019	0.0066	0.0660	0.0006	0.71	
temora		TEM 165.4	64.6	11.2	0.40	0.4	0.07	0.0000373	0.0536	0.0006	0.1243	0.0020	0.5094	0.0073	0.0659	0.0006	0.61	
temora		TEM 170.9	84.7	11.7	0.51	0.5	0.09	0.0000490	0.0521	0.0010	0.0907	0.0024	0.4796	0.0067	0.0649	0.0005	0.58	
temora		TEM 126.4	37.6	8.2	0.31	0.9	0.25	0.0001341	0.0536	0.0008	0.1292	0.0026	0.4946	0.0087	0.0669	0.0006	0.41	
temora		TEM 131.5	53.8	9.0	0.42	0.7	0.16	0.0000870	0.0536	0.0008	0.1499	0.0021	0.5106	0.0148	0.0669	0.0011	0.57	
temora		TEM 150.5	72.4	10.5	0.49	0.3	0.07	0.0000364	0.0554	0.0013	0.1499	0.0021	0.5164	0.0101	0.0664	0.0007	0.55	
temora		162	113.7	34.1	7.5	0.31	0.0	0.00	0.0000002	0.0542	0.0012	0.0796	0.0021	0.4971	0.0117	0.0665	0.0007	0.42
temora		171	108.6	28.6	7.1	0.27	0.4	0.12	0.0000649	0.0540	0.0012	0.0796	0.0021	0.4971	0.0117	0.0665	0.0007	0.42
temora		180	59.7	21.5	4.0	0.37	0.6	0.34	0.0001832	0.0544	0.0019	0.1110	0.0048	0.4945	0.0192	0.0664	0.0010	0.38
temora		189	80.0	27.5	5.3	0.35	0.7	0.28	0.0001512	0.0544	0.0014	0.1065	0.0039	0.4898	0.0140	0.0653	0.0007	0.37
temora		198	46.6	16.4	3.1	0.36	0.0	0.00	0.0000004	0.0564	0.0009	0.1141	0.0022	0.5085	0.0100	0.0654	0.0007	0.42
temora		207	65.9	22.9	4.4	0.36	0.1	0.03	0.00000182	0.0569	0.0011	0.1158	0.0017	0.5191	0.0117	0.0661	0.0008	0.52
temora		216	90.8	49.5	6.3	0.56	2.0	0.76	0.0004101	0.0516	0.0017	0.1506	0.0070	0.4555	0.0153	0.0640	0.0007	0.31
temora		225	128.1	60.7	8.8	0.49	0.9	0.23	0.0001259	0.0537	0.0012	0.1446	0.0031	0.4881	0.0117	0.0659	0.0007	0.42
temora		238	93.9	46.1	6.4	0.50	0.8	0.30	0.0001599	0.0534	0.0013	0.1509	0.0037	0.4790	0.0126	0.0650	0.0008	0.45
temora		TEM 131.5	53.8	9.0	0.42	0.7	0.16	0.0000870	0.0536	0.0008	0.1292	0.0026	0.4946	0.0087	0.0669	0.0006	0.50	
temora		TEM 150.5	72.4	10.5	0.49	0.3	0.07	0.0000364	0.0554	0.0013	0.1499	0.0021	0.5106	0.0148	0.0669	0.0011	0.55	
temora		162	113.7	34.1	7.5	0.31	0.0	0.00	0.0000002	0.0542	0.0012	0.0796	0.0021	0.4971	0.0117	0.0665	0.0007	0.42
temora		171	108.6	28.6	7.1	0.27	0.4	0.12	0.0000649	0.0544	0.0019	0.1110	0.0048	0.4945	0.0192	0.0664	0.0010	0.38
temora		180	59.7	21.5	4.0	0.37	0.6	0.34	0.0001832	0.0544	0.0014	0.1065	0.0039	0.4898	0.0140	0.0653	0.0007	0.37
temora		189	80.0	27.5	5.3	0.35	0.7	0.28	0.0001512	0.0544	0.0014	0.1065	0.0039	0.4898	0.0140	0.0653	0.0007	0.37
temora		198	46.6	16.4	3.1	0.36	0.0	0.00	0.0000004	0.0564	0.0009	0.1141	0.0022	0.5085	0.0100	0.0654	0.0007	0.42
temora		207	65.9	22.9	4.4	0.36	0.1	0.03	0.00000182	0.0569	0.0011	0.1158	0.0017	0.5191	0.0117	0.0661	0.0008	0.52
temora		216	90.8	49.5	6.3	0.56	2.0	0.76	0.0004101	0.0516	0.0017	0.1506	0.0070	0.4555	0.0153	0.0640	0.0007	0.31
temora		225	128.1	60.7	8.8	0.49	0.9	0.23	0.0001259	0.0537	0.0012	0.1446	0.0031	0.4881	0.0117	0.0659	0.0007	0.42
temora		238	93.9	46.1	6.4	0.50	0.8	0.30	0.0001599	0.0534	0.0013	0.1509	0.0037	0.4790	0.0126	0.0650	0.0008	0.45
temora		TEM 131.5	53.8	9.0	0.42	0.7	0.16	0.0000870	0.0536	0.0008	0.1292	0.0026	0.4946	0.0087	0.0669	0.0006	0.50	
temora		162	113.7	34.1	7.5	0.31	0.0	0.00	0.0000002	0.0542	0.0012	0.0796	0.0021	0.4971	0.0117	0.0665	0.0007	0.42
temora		171	108.6	28.6	7.1	0.27	0.4	0.12	0.0000649	0.0544	0.0019	0.1110	0.0048	0.4945	0.0192	0.0664	0.0010	0.38
temora		180	59.7	21.5	4.0	0.37	0.6	0.34	0.0001832	0.0544	0.0014	0.1065	0.0039	0.4898	0.0140	0.0653	0.0007	0.37
temora		189	80.0	27.5	5.3	0.35	0.7	0.28	0.0001512	0.0544	0.0014	0.1065	0.0039	0.4898	0.0140	0.0653	0.0007	0.37
temora		198	46.6	16.4	3.1	0.36	0.0	0.00	0.0000004	0.0564	0.0009	0.1141	0.0022	0.5085	0.0100	0.0654	0.0007	0.42
temora		207	65.9	22.9	4.4	0.36	0.1	0.03	0.00000182	0.0569	0.0011	0.1158	0.0017	0.5191	0.0117	0.0661	0.0008	0.52
temora		216	90.8	49.5	6.3	0.56	2.0	0.76	0.0004101	0.0516	0.0017	0.150						

Appendix 4d  
Zircon oxygen isotope data and average values of bracketing zircon standard 91500

analyses no.	grain no.	$^{18}\text{O}/^{16}\text{O}$ (measured)	2SD	1 s.e.m.	$\delta^{18}\text{O}$ [‰] VSMOW	2SD	1 s.e.m.	n	grain area	comment
<u>Session 11 (04.06.2005)</u>										
91500-3 - 1-9		0.0020133	0.0000011	0.0000002	10.02	0.54	0.090	9		
91500-3 - 11-15, 17-18, 20		0.0020127	0.0000006	0.0000001	9.68	0.28	0.049	8		
Kemnay	SA04/07 - 1	1	0.0020091	0.0000003	7.9	0.101			c1	
	SA04/07 - 2	2	0.0020099	0.0000003	8.3	0.124			c1	
	SA04/07 - 4	2	0.0020094	0.0000004	8.1	0.147			rim	
	SA04/07 - 6	4	0.0020036	0.0000002	5.2	0.049			c1	rejected, grain plucked
	SA04/07 - 7	4	0.0020054	0.0000002	6.1	0.065			rim	rejected, grain plucked
	SA04/07 - 9	5	0.0020075	0.0000002	7.1	0.060			c2	
	SA04/07 - 10	5	0.0020049	0.0000002	5.8	0.065			c1	rejected, crack
	SA04/07 - 11	6	0.0020091	0.0000002	7.9	0.071			c1	rejected, crack
	SA04/07 - 12	6	0.0020089	0.0000003	7.8	0.121			c2	rejected, crack
	SA04/07 - 15	8	0.0020089	0.0000004	7.8	0.139			c1	rejected, crack
	91500-3 - 21-25		0.0020127	0.0000008	0.0000002	9.69	0.37	0.084	5	
	SA04/07 - 16	8	0.0020093	0.0000003	8.0	0.100			c2	rejected, crack
	SA04/07 - 18	9	0.0020087	0.0000004	7.7	0.147			c1	
	SA04/07 - 19	9	0.0020115	0.0000002	9.1	0.090			c2	
	SA04/07 - 22	11	0.0020022	0.0000002	4.5	0.053			c1	rejected, grain plucked
	SA04/07 - 23	11	0.0020069	0.0000003	6.8	0.099			rim	rejected, grain plucked
	SA04/07 - 24	12	0.0020073	0.0000003	7.0	0.091			c1	
	SA04/07 - 26	13	0.0020067	0.0000003	6.7	0.092			inh	
	SA04/07 - 27	13	0.0020088	0.0000002	7.8	0.079			rim	
	SA04/07 - 33	16	0.0020066	0.0000003	6.7	0.093			c1	
	SA04/07 - 34	16	0.0020074	0.0000003	7.1	0.113			rim	rejected, grain plucked
	91500-3 - 26-30		0.0020133	0.0000006	0.0000001	10.01	0.28	0.062	5	
	SA04/07 - 37	18	0.0020106	0.0000003	8.6	0.110			c1	
	SA04/07 - 38	18	0.0020125	0.0000003	9.6	0.128			c1+rim	
	SA04/07 - 39	19	0.0020109	0.0000002	8.8	0.089			c1	rejected, crack
	SA04/07 - 40	19	0.0020107	0.0000003	8.7	0.131			c2	rejected, crack
	SA04/07 - 46	22	0.0020125	0.0000003	9.6	0.143			c1	
	SA04/07 - 47	22	0.0020106	0.0000003	8.7	0.146			rim	rejected, crack
	SA04/07 - 48	23	0.0020092	0.0000004	7.9	0.176			inh	
	SA04/07 - 49	23	0.0020082	0.0000004	7.5	0.140			rim	
	SA04/07 - 50	24	0.0020146	0.0000004	10.6	0.188			c2a	
	SA04/07 - 51	24	0.0020130	0.0000003	9.9	0.151			c2b	
	91500-3 - 31-32, 35		0.0020131	0.0000011	0.0000003	9.90	0.57	0.164	3	
<u>Session 12 (05.06.2005)</u>										
91500-18 - 60-69		0.0020107	0.0000018	0.0000003	9.85	0.91	0.151	10		
91500-3 - 82-91		0.0020104	0.0000010	0.0000002	9.68	0.48	0.076	10		
SA04/07 - 55	26	0.0020084		0.0000004	8.7		0.160		inh	rejected, correction on position of secondary ion beam anomalously large
SA04/07 - 56	26	0.0020152		0.0000004	12.1		0.211		rim	rejected, crack
SA04/07 - 59	28	0.0020134		0.0000005	11.2		0.250		inh	
SA04/07 - 60	28	0.0020121		0.0000007	10.5		0.358		rim	
SA04/07 - 61	29	0.0020110		0.0000004	10.0		0.176		c1	rejected, crack
SA04/07 - 62	29	0.0020126		0.0000003	10.8		0.141		rim	
SA04/07 - 63	30	0.0020159		0.0000004	12.4		0.219		c2	
SA04/07 - 72	33	0.0020151		0.0000006	12.0		0.337		c2	
SA04/07 - 73	33	0.0020150		0.0000004	12.0		0.224		rim	
SA04/07 - 74	34	0.0020166		0.0000002	12.8		0.152		c2c	rejected, crack
SA04/07 - 75	34	0.0020144		0.0000003	11.7		0.195		rim	
91500-3 - 93-96		0.0020111	0.0000006	0.0000002	10.05	0.30	0.076	4		
SA04/07 - 76	34	0.0020117		0.0000003	10.3		0.170		c2b	rejected, correction on position of secondary ion beam anomalously large
SA04/07 - 77	34	0.0020143		0.0000003	11.6		0.200		c2a	rejected, crack
SA04/07 - 78	35	0.0020176		0.0000005	13.3		0.331		inh1	
SA04/07 - 79	35	0.0020150		0.0000003	12.0		0.154		inh2	
SA04/07 - 80	35	0.0020137		0.0000002	11.3		0.137		r1	
SA04/07 - 81	35	0.0020131		0.0000004	11.0		0.192		r2	rejected, crack
Cove	SA04/10 - 2	2	0.0020104	0.0000005	9.7	0.225			c1	rejected, correction on position of secondary ion beam anomalously large
	SA04/10 - 3	3	0.0020094	0.0000003	9.2	0.119			c1	rejected, crack
	SA04/10 - 7	5	0.0020091	0.0000002	9.0	0.111			rim	rejected, crack
	SA04/10 - 8	5	0.0020095	0.0000003	9.3	0.155			c2c	
	91500-3 - 97-101		0.0020110	0.0000011	0.0000002	9.98	0.43	0.097	5	
	SA04/10 - 13	7	0.0020115	0.0000002	10.3	0.095			c1	
	SA04/10 - 14	7	0.0020120	0.0000003	10.5	0.153			rim	
	SA04/10 - 15	8	0.0020094	0.0000002	9.2	0.103			inh	rejected, crack
	SA04/10 - 16	8	0.0020086	0.0000003	8.8	0.137			inh	rejected, crack
	SA04/10 - 17	9	0.0020090	0.0000002	9.0	0.111			inh	
	SA04/10 - 18	9	0.0020114	0.0000002	10.2	0.117			rim	rejected, crack
	SA04/10 - 23	12	0.0020054	0.0000004	7.2	0.152			inh	rejected, crack
	SA04/10 - 22	12	0.0020068	0.0000002	7.9	0.082			inh	
	SA04/10 - 24	12	0.0020142	0.0000002	11.6	0.110			rim	
	SA04/10 - 39	18	0.0020103	0.0000003	9.6	0.123			rim	rejected, crack
91500-3 - 102-106		0.0020112	0.0000007	0.0000002	10.09	0.34	0.085	5		

analyses no.	grain no.	$^{18}\text{O}/^{16}\text{O}$ (measured)	2SD	1 s.e.m.	$\delta^{18}\text{O}$ [‰] VSMOW	2SD	1 s.e.m. n	grain area	comment
SA04/10 - 41	18	0.0020060		0.0000003	6.9		0.116	inh1	rejected, crack
SA04/10 - 42	18	0.0020060		0.0000003	6.9		0.090	inh2	
SA04/10 - 43	19	0.0020091		0.0000003	8.4		0.139	c2b	rejected, crack
SA04/10 - 44	19	0.0020086		0.0000003	8.2		0.107	c2c	rejected, crack
SA04/10 - 45	19	0.0020104		0.0000002	9.1		0.090	c2a	
SA04/10 - 46	20	0.0020061		0.0000004	6.9		0.155	inh	
SA04/10 - 47	20	0.0020051		0.0000002	6.5		0.058	inh	rejected, > 20 % discordant
SA04/10 - 48	20	0.0020111		0.0000003	9.4		0.139	rim	
<b>Nigg Bay</b> SA04/11 - 3	2	0.0020053		0.0000002	6.5		0.068	c1	rejected, correction on position of secondary ion beam anomalously large
SA04/11 - 4	2	0.0020045		0.0000005	6.2		0.148	rim	rejected, crack
<u>Session 13 (05.06.2005)</u>									
91500-3 - 107-111		0.0020117	0.0000005	0.0000001	9.75	0.26	0.057	5	
SA04/11 - 5	3	0.0020011		0.0000003	4.5		0.067	inh	rejected, correction on position of secondary ion beam anomalously large
SA04/11 - 6	3	0.0020003		0.0000002	4.1		0.050	inh	
SA04/11 - 10	5	0.0020033		0.0000002	5.6		0.052	inh	
SA04/11 - 11	5	0.0020029		0.0000003	5.4		0.091	inh	rejected, crack
SA04/11 - 15	7	0.0020008		0.0000002	4.3		0.048	?	rejected, crack
SA04/11 - 21	10	0.0020025		0.0000004	5.2		0.114	inh	rejected, crack
SA04/11 - 22	10	0.0020011		0.0000003	4.5		0.062	inh	rejected, crack
SA04/11 - 32	14	0.0020075		0.0000004	7.7		0.153	rim	rejected, crack
SA04/11 - 33	14	0.0020028		0.0000003	5.3		0.074	inh	
SA04/11 - 34	14	0.0020034		0.0000002	5.6		0.067	inh	rejected, crack
91500-3 - 112-116		0.0020122	0.0000001	0.0000000	10.00	0.07	0.016	5	
SA04/11 - 35	15	0.0020017		0.0000004	4.8		0.085	c2a	
SA04/11 - 36	15	0.0020020		0.0000004	4.9		0.100	c2b	
SA04/11 - 37	16	0.0020085		0.0000003	8.1		0.135	c2	rejected, crack
SA04/11 - 38	16	0.0020035		0.0000004	5.7		0.117	rim	rejected, > 20 % discordant
SA04/11 - 40	17	0.0020075		0.0000003	7.6		0.111	c2a	
SA04/11 - 41	17	0.0020061		0.0000002	7.0		0.073	c2b	
SA04/11 - 42	17	0.0020071		0.0000003	7.5		0.113	rim	rejected, crack
SA04/11 - 47	19	0.0020071		0.0000003	7.5		0.105	rim	
SA04/11 - 48	19	0.0020034		0.0000005	5.6		0.142	inh	rejected, crack
SA04/11 - 49	19	0.0020039		0.0000002	5.9		0.067	inh	
<u>Session 14 (05.06.2005)</u>									
91500-3 - 117-121		0.0020106	0.0000016	0.0000003	9.84	0.67	0.151	5	
SA04/11 - 52	21	0.0020023		0.0000002	5.7		0.064	inh	rejected, correction on position of secondary ion beam anomalously large
SA04/11 - 53	21	0.0020061		0.0000003	7.6		0.100	rim	
SA04/11 - 66	25	0.0020038		0.0000002	6.5		0.076	inh	
SA04/11 - 99	25	0.0020048		0.0000003	7.0		0.110	rim	
SA04/11 - 67	26	0.0020073		0.0000003	8.2		0.128	rim	rejected, crack
SA04/11 - 68	26	0.0020062		0.0000003	7.7		0.123	inh	
SA04/11 - 69	26	0.0020081		0.0000003	8.6		0.121	inh	rejected, crack
SA04/11 - 73	28	0.0020068		0.0000005	8.0		0.180	rim	
SA04/11 - 74	28	0.0020049		0.0000003	7.0		0.122	rim	
SA04/11 - 75	29	0.0020047		0.0000002	6.9		0.069	c1	
91500-3 - 122-126		0.0020107	0.0000016	0.0000003	9.88	0.56	0.126	5	
SA04/11 - 76	29	0.0020049		0.0000004	7.0		0.125	rim	rejected, correction on position of secondary ion beam anomalously large
SA04/11 - 81	31	0.0020040		0.0000003	6.6		0.114	inh	
SA04/11 - 82	31	0.0020040		0.0000003	6.6		0.082	rim	
SA04/11 - 86	33	0.0020103		0.0000002	9.7		0.083	inh	
SA04/11 - 87	33	0.0020047		0.0000004	6.9		0.138	inh	rejected, crack
SA04/11 - 88	34	0.0020025		0.0000003	5.8		0.075	inh	
SA04/11 - 89	34	0.0020063		0.0000004	7.7		0.156	rim	rejected, crack
SA04/11 - 90	35	0.0020025		0.0000002	5.8		0.055	inh	
SA04/11 - 91	35	0.0020031		0.0000004	6.1		0.109	inh	
SA04/11 - 92	35	0.0020031		0.0000005	6.1		0.164	rim	
<u>Session 15 (05.06.2005)</u>									
91500 - 127-131		0.0020095	0.0000009	0.0000002	9.87	0.5	0.102	5	
SA04/11 - 97	38	0.0020016	0.0000004	0.0000004	5.9		0.129	inh	rejected, correction on position of secondary ion beam anomalously large
SA04/11 - 98	38	0.0020066	0.0000003	8.4			0.121	rim	
91500 - 132-135		0.0020097	0.0000007	0.0000002	9.99	0.3	0.082	4	
91500 - 137, 139-141		0.0020092	0.0000005	0.0000001	9.71	0.3	0.064	4	

c1 = unzoned inner core  
c2 = oscillatory zoned outer core  
r1-2 = rim

## Appendix 4e

Hf and Yb isotopes and their ratios in the rocks from the Nigg Bay area																							
grain no.	grain area	age	1 SD	$\delta^{18}\text{O}$ ‰	$2\sigma$	$^{176}\text{Lu}/^{177}\text{Hf}$ (WR)	Hf total	Yb/Hf	$^{178}\text{Hf}/^{177}\text{Hf}$	1s%	$^{176}\text{Hf}/^{177}\text{Hf}$	1s%	$^{176}\text{Yb}/^{177}\text{Hf}$	1s%	$^{176}\text{Lu}/^{177}\text{Hf}$	1s%	$^{176}\text{Hf}/^{177}\text{Hf}$ (initial)	$\epsilon_{\text{Hf}}$	95% conf.	TDM <sub>C</sub>	95% conf.	TDM <sub>N</sub>	95% conf.
Kennay																							
1	c1	457	4	7.9	0.6	0.004	7.40	0.06	1.467180	0.0074	0.282124	0.0110	0.14833	8.2	0.00037	8.2	0.282121	-13.0	1.2	2259	73	1690	49
9	c1	457	4	7.7	0.6	0.004	5.18	0.05	1.467270	0.0080	0.282211	0.0146	0.13516	7.8	0.00037	7.9	0.282208	-9.9	1.6	2066	95	1557	64
24	c2	457	4	10.6	0.6	0.004	6.05	0.05	1.467330	0.0032	0.282036	0.0059	0.13219	7.8	0.00039	7.6	0.282033	-16.1	0.7	2454	40	1824	26
23	inh	457	4	7.9	0.6	0.004	6.00	0.05	1.467240	0.0035	0.282206	0.0067	0.13606	7.0	0.00040	7.1	0.282203	-10.1	0.8	1716	58	1496	40
25	inh	457	4	7.50	0.07	0.004	7.50	0.07	1.467230	0.0036	0.281737	0.0092	0.17200	7.1	0.00047	7.2	0.281703	-26.7	1.0	2333	70	2127	63
26	inh	457	4	8.7	0.6	0.004	6.17	0.05	1.467260	0.0038	0.282235	0.0072	0.13099	7.3	0.00043	7.4	0.282232	-9.0	0.8	1647	61	1450	41
28	rim	457	4	11.2	0.6	0.004	6.84	0.08	1.467200	0.0036	0.282121	0.0062	0.21221	12.9	0.00057	13.3	0.282116	-13.2	0.7	2270	43	1697	28
31	inh	457	4		0.004	8.46	0.13	1.467260	0.0041	0.281988	0.0077	0.33110	7.2	0.00092	7.3	0.281980	-18.0	0.9	1934	63	1775	69	
36	c2	457	4		0.004	5.94	0.07	1.467260	0.0038	0.282159	0.0058	0.19016	7.8	0.00053	7.8	0.282155	-11.8	0.7	2185	40	1638	27	
35	inh	457	4	13.3	0.6	0.004	6.50	0.05	1.467280	0.0034	0.281662	0.0074	0.13339	11.4	0.00031	11.2	0.281660	-29.3	0.8	2456	59	2233	50
40	c2	457	4		0.004	6.41	0.05	1.467270	0.0035	0.282161	0.0069	0.12671	8.1	0.00033	8.8	0.282158	-11.7	0.8	2176	47	1633	31	
37	c2	457	4		0.004	5.98	0.08	1.467240	0.0035	0.282170	0.0060	0.20786	7.5	0.00054	7.6	0.282166	-11.4	0.7	2160	41	1622	27	
18	c1	457	4	8.6	0.6	0.004	5.29	0.06	1.467090	0.0093	0.282105	0.0120	0.14372	9.5	0.00035	8.6	0.282102	-14.3	1.3	2301	73	1718	53
23	inh	457	4	7.5	0.6	0.004	9.91	0.19	1.467280	0.0044	0.282099	0.0077	0.47027	7.0	0.00122	7.0	0.282089	-14.1	0.9	2331	59	1739	35
(2)	rim	457	4	7.5	0.6	0.004	2.67		1.467570	0.0074	0.282178	0.0167	0.59385	7.1	0.00223	7.1	0.282159	-11.6	1.8	2175	110	1632	74
33	inh	457	4	12.4	0.6	0.004	6.40	0.09	1.467240	0.0043	0.281790	0.0089	0.20370	7.0	0.00050	7.1	0.281786	-24.8	1.0	2389	71	2083	58
33	rim	457	4	12.0	0.6	0.004	3.71	0.31	1.467240	0.0064	0.282024	0.0177	0.97430	7.1	0.00306	7.1	0.281998	-17.3	1.9	2531	116	1877	79
Cove																							
5	c2	458	7	9.3	0.6	0.004	4.41	0.03	1.467260	0.0038	0.282134	0.0074	0.08757	9.1	0.00023	9.0	0.282132	-12.6	0.9	2234	52	1672	33
9	inh	458	7	9.0	0.6	0.004	5.32	0.05	1.467280	0.0032	0.282190	0.0072	0.11826	7.1	0.00032	7.3	0.282188	-10.6	0.9	1796	55	1529	39
17	inh	458	7		0.004	6.83	0.04	1.467220	0.0034	0.282124	0.0060	0.11231	7.4	0.00028	7.3	0.282122	-12.9	0.8	1825	62	1606	38	
17	rim	458	7		0.004	10.45	0.07	1.467240	0.0038	0.282072	0.0058	0.18960	7.6	0.00050	7.9	0.282068	-14.8	0.7	2376	42	1770	27	
19	c2	458	7		0.004	4.52	0.06	1.467230	0.0036	0.282052	0.0072	0.14044	7.1	0.00033	7.2	0.282049	-15.5	0.9	2417	50	1799	32	
21	rim	458	7		0.004	6.97	0.11	1.467240	0.0035	0.282079	0.0064	0.27602	7.1	0.00076	7.1	0.282073	-14.7	0.8	2366	46	1763	29	
27	c1	458	7	10.3	0.6	0.004	5.96	0.36	1.467260	0.0040	0.282037	0.0107	1.14409	7.9	0.00265	7.8	0.282015	-26.7	1.3	2494	75	1851	49
12	inh	458	7	11.6	0.6	0.004	7.72	0.10	1.467110	0.0051	0.281915	0.0092	0.10142	9.3	0.00025	8.4	0.281913	-20.3	1.1	2718	62	2005	41
14	c1	458	7		0.004	7.04	0.07	1.467240	0.0038	0.282115	0.0072	0.16782	9.2	0.00047	9.5	0.282111	-13.3	0.9	2281	50	1704	32	
20	inh	458	7		0.004	6.38	0.03	1.467250	0.0063	0.281105	0.0067	0.04461	7.2	0.00013	7.1	0.281104	-49.0	0.8	3737	59	3094	38	
Nigg Bay																							
3	inh	465	5	4.5	0.6	0.003	6.59	0.11	1.467060	0.0062	0.282149	0.0163	0.26913	7.1	0.00064	7.1	0.282144	-12.0	1.8	1799	128	1576	90
25	inh	465	5	6.5	0.6	0.003	5.42	0.04	1.467290	0.0042	0.282201	0.0069	0.09024	7.0	0.00024	7.0	0.282199	-10.0	0.8	1662	67	1490	41
25	rim	465	5	7.0	0.6	0.003	5.02	0.11	1.467390	0.0046	0.282049	0.0086	0.28335	8.2	0.00101	9.3	0.282040	-15.7	1.0	2433	59	1774	38
28	inh	465	5	7.0	0.6	0.003	4.86	0.04	1.467250	0.0035	0.282216	0.0067	0.09736	8.1	0.00025	8.0	0.282214	-9.5	0.8	1718	59	1485	37
28	rim	465	5	8.0	0.6	0.003	8.80	0.10	1.467240	0.0034	0.281966	0.0062	0.26380	7.0	0.00067	7.0	0.282190	-18.5	0.7	2609	43	1892	27
31	rim	465	5	6.6	0.6	0.003	7.42	0.10	1.467290	0.0035	0.282031	0.0069	0.24363	7.2	0.00065	8.4	0.282026	-16.2	0.8	2466	48	1796	30
31	rim	465	5	6.6	0.6	0.003	4.83	0.06	1.467290	0.0036	0.282099	0.0064	0.14142	7.4	0.00036	7.3	0.282096	-13.7	0.8	2250	88	2259	554
5	rim	465	5	6.6	0.6	0.003	6.01	0.09	1.467160	0.0061	0.282142	0.0086	0.19840	8.6	0.00047	8.7	0.282138	-12.2	1.0	2817	58	1629	37

**Appendix 4f**  
**Hf isotope data of Mud Tank zircon standard**

	total Hf	1σ	Yb/Hf	1σ	$^{176}\text{Yb}/^{176}\text{Hf}$	1σ	$^{176}\text{Lu}/^{176}\text{Hf}$	1σ	$^{176}\text{Hf}/^{177}\text{Hf}$	1σ
08/02/07										
Mud Tank 1	5.9	0.06	0.007	0.000052	0.017588	0.000130	0.0002956	0.0000006	0.282508	0.000012
Mud Tank 2	6.0	0.07	0.007	0.000043	0.017752	0.000110	0.0003006	0.0000003	0.282486	0.000010
Mud Tank 3	6.2	0.11	0.007	0.000035	0.017047	0.000088	0.0002987	0.0000006	0.282514	0.000012
Mud Tank 4	6.2	0.10	0.007	0.000030	0.016695	0.000075	0.0002905	0.0000005	0.282513	0.000012
Mud Tank 5	6.2	0.11	0.007	0.000038	0.017507	0.000095	0.0003028	0.0000006	0.282498	0.000010
Mud Tank 6	4.9	0.10	0.007	0.000034	0.018183	0.000085	0.0003054	0.0000005	0.282515	0.000010
Mud Tank 7	5.3	0.10	0.007	0.000034	0.017745	0.000086	0.0003025	0.0000005	0.282499	0.000012
Mud Tank 8	4.5	0.07	0.007	0.000041	0.018170	0.000100	0.0003037	0.0000006	0.282492	0.000012
Mud Tank 9	4.9	0.09	0.007	0.000044	0.018256	0.000110	0.0003046	0.0000005	0.282486	0.000010
Mud Tank 10	4.7	0.09	0.007	0.000032	0.017485	0.000081	0.0002925	0.0000007	0.282537	0.000013
Mud Tank 11	5.2	0.09	0.007	0.000036	0.016926	0.000091	0.0002910	0.0000005	0.282518	0.000012
Mud Tank 12	5.1	0.06	0.008	0.000060	0.019555	0.000150	0.0003241	0.0000008	0.282527	0.000013
Mud Tank 13	5.5	0.06	0.008	0.000040	0.019314	0.000099	0.0003218	0.0000006	0.282506	0.000013
Mud Tank 14	4.7	0.08	0.008	0.000079	0.019078	0.000200	0.0003131	0.0000007	0.282513	0.000013
Mud Tank 15	5.4	0.06	0.007	0.000051	0.018439	0.000130	0.0003052	0.0000007	0.282512	0.000010
Mud Tank 16	5.7	0.05	0.007	0.000053	0.017897	0.000130	0.0002976	0.0000005	0.282510	0.000011
Mud Tank 17	5.8	0.06	0.005	0.000040	0.013722	0.000100	0.0002295	0.0000006	0.282505	0.000009
Mud Tank 18	6.1	0.13	0.006	0.000042	0.015670	0.000110	0.0002612	0.0000007	0.282535	0.000011
Mud Tank 19	6.1	0.13	0.007	0.000051	0.017408	0.000130	0.0002881	0.0000005	0.282509	0.000012
Mud Tank 20	6.1	0.10	0.006	0.000047	0.016142	0.000120	0.0002672	0.0000005	0.282521	0.000009
Mud Tank 21	5.9	0.05	0.007	0.000052	0.016741	0.000130	0.0002779	0.0000005	0.282530	0.000013
Mud Tank 22	5.5	0.06	0.007	0.000052	0.016853	0.000130	0.0002804	0.0000008	0.282513	0.000011
Mud Tank 23	5.2	0.08	0.007	0.000058	0.017852	0.000150	0.0002953	0.0000006	0.282511	0.000016
Mud Tank 24	4.6	0.08	0.007	0.000062	0.017262	0.000160	0.0002815	0.0000008	0.282540	0.000014
Mud Tank 25	5.3	0.09	0.006	0.000030	0.015944	0.000076	0.0002574	0.0000005	0.282508	0.000010
Mud Tank 26	5.7	0.10	0.007	0.000033	0.017936	0.000082	0.0002951	0.0000004	0.282525	0.000012
average (n=48)	5.5		0.007		0.017430		0.000292		0.282513	
2SD	1.1		0.001		0.002432		0.000041		0.000028	

#### Appendix 4g

##### Two-component magma mixing modelling

% Dalradian	$\delta^{18}\text{O}$ [‰]	$\epsilon\text{Hf}_T$	$\epsilon\text{Hf}_C$	% enriched mantle
0	5.5*	1.3*	3.4*	1
0.1	6.4	-0.5	1.4	0.9
0.2	7.2	-2.3	-0.7	0.8
0.3	8.1	-4.2	-2.7	0.7
0.4	9.0	-6.0	-4.7	0.6
0.5	9.9	-7.8	-6.8	0.5
0.6	10.7	-9.6	-8.8	0.4
0.7	11.6	-11.4	-10.8	0.3
0.8	12.5	-13.3	-12.8	0.2
0.9	13.3	-15.1	-14.9	0.1
1	14.2*	-16.9*	-16.9*	0

% Appin Group	$\delta^{18}\text{O}$ [‰]	$\epsilon\text{Hf}_T$	$\epsilon\text{Hf}_C$	% enriched mantle
0	5.5	1.3	3.4	1
0.1	6.1	0.2	2.1	0.9
0.2	6.7	-1.0	0.7	0.8
0.3	7.3	-2.1	-0.7	0.7
0.4	7.9	-3.3	-2.0	0.6
0.5	8.5	-4.4	-3.4	0.5
0.6	9.0	-5.5	-4.7	0.4
0.7	9.6	-6.7	-6.1	0.3
0.8	10.2	-7.8	-7.4	0.2
0.9	10.8	-9.0	-8.8	0.1
1	11.4	-10.1	-10.1	0

% Argyll Group	$\delta^{18}\text{O}$ [‰]	$\epsilon\text{Hf}_T$	$\epsilon\text{Hf}_C$	% enriched mantle
0	5.5	1.3	3.4	1
0.1	6.5	-1.1	0.8	0.9
0.2	7.4	-3.4	-1.7	0.8
0.3	8.4	-5.8	-4.3	0.7
0.4	9.3	-8.1	-6.9	0.6
0.5	10.3	-10.5	-9.5	0.5
0.6	11.3	-12.9	-12.0	0.4
0.7	12.2	-15.2	-14.6	0.3
0.8	13.2	-17.6	-17.2	0.2
0.9	14.1	-19.9	-19.7	0.1
1	15.1	-22.3	-22.3	0

% Appin Group	$\delta^{18}\text{O}$ [‰]	$\epsilon\text{Hf}_T$	% Argyll
0	15.1	-22.3	1
0.1	14.7	-21.1	0.9
0.2	14.4	-19.9	0.8
0.3	14.0	-18.6	0.7
0.4	13.6	-17.4	0.6
0.5	13.3	-16.2	0.5
0.6	12.9	-15.0	0.4
0.7	12.5	-13.8	0.3
0.8	12.1	-12.5	0.2
0.9	11.8	-11.3	0.1
1	11.4	-10.1	0

\*Average enriched mantle and average Dalradian

(data from Anderson et al., 2004; Canning et al., 1998; Eiler, 2001; Frost and O'Nions, 1985; O'Nions et al., 1983; Thirlwall, 1982)

$\epsilon\text{Hf}_T$  = data from Thirlwall (1982)

$\epsilon\text{Hf}_C$  = data from Canning et al. (1998)